TEXTILES PAPER LEATHER

AMERICAN DYESTUFF REPORTER

Including the Proceedings of the
AMERICAN ASSOCIATION OF TEXTILE CHEMISTS AND COLORISTS

VOLUME XII JANUARY 1, 1923 NUMBER 1

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Deal Direct with the Manufacturer

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for the

Textile Industry

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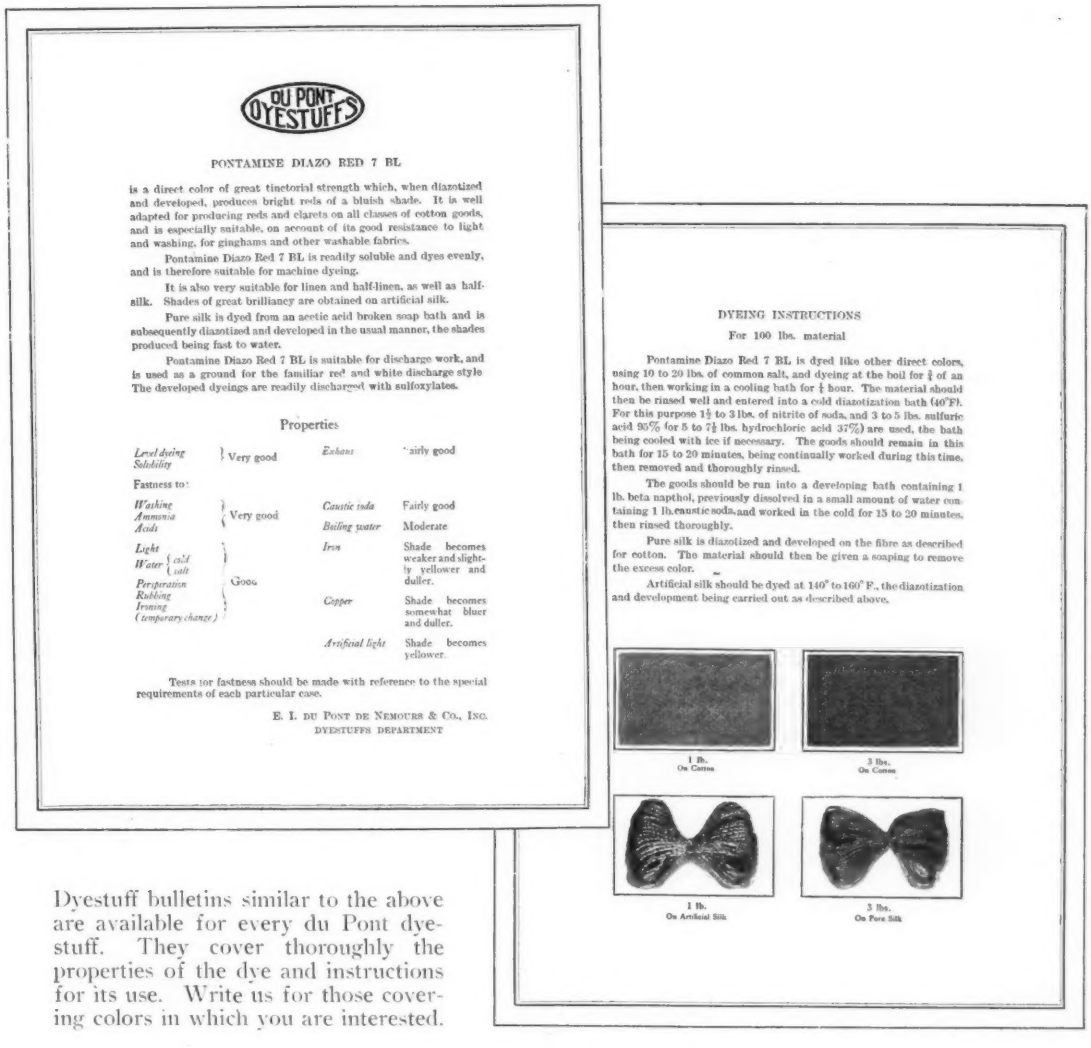

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Light	Good	*Iron*	Shade becomes weaker and slightly yellower and duller.
Water { *cold*			
{ *salt*			
Perspiration			
Rubbing		*Copper*	Shade becomes somewhat bluer and duller.
Ironing (*temporary change*)			
		Artificial light	Shade becomes yellower.

Tests for fastness should be made with reference to the special requirements of each particular case.

E. I. DU PONT DE NEMOURS & CO., INC.
DYESTUFFS DEPARTMENT

DYEING INSTRUCTIONS

For 100 lbs. material

Pontamine Diazo Red 7 BL is dyed like other direct colors, using 10 to 20 lbs. of common salt, and dyeing at the boil for ½ of an hour, then working in a cooling bath for ½ hour. The material should then be rinsed well and entered into a cold diazotization bath (40°F). For this purpose 1½ to 3 lbs. of nitrite of soda, and 3 to 5 lbs. sulfuric acid 96% for 5 to 7½ lbs. hydrochloric acid 37%) are used, the bath being cooled with ice if necessary. The goods should remain in this bath for 15 to 20 minutes, being continually worked during this time, then removed and thoroughly rinsed.

The goods should be run into a developing bath containing 1 lb. beta napthol, previously dissolved in a small amount of water containing 1 lb. caustic soda, and worked in the cold for 15 to 20 minutes, then rinsed thoroughly.

Pure silk is diazotized and developed on the fibre as described for cotton. The material should then be given a soaping to remove the excess color.

Artificial silk should be dyed at 140° to 160° F., the diazotization and development being carried out as described above.

1 lb. On Cotton

3 lbs. On Cotton

1 lb. On Artificial Silk

3 lbs. On Pure Silk

Dyestuff bulletins similar to the above are available for every du Pont dyestuff. They cover thoroughly the properties of the dye and instructions for its use. Write us for those covering colors in which you are interested.

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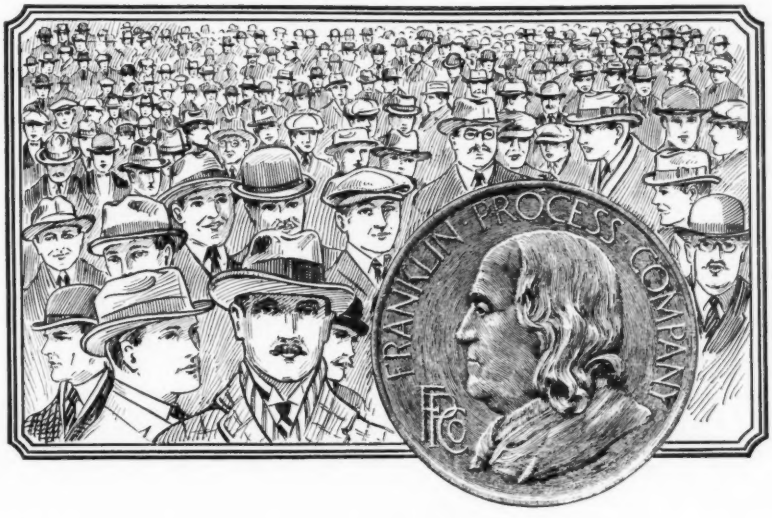

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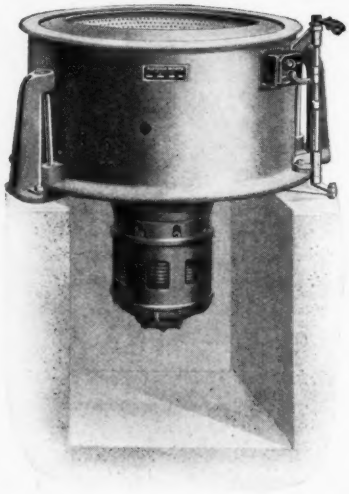

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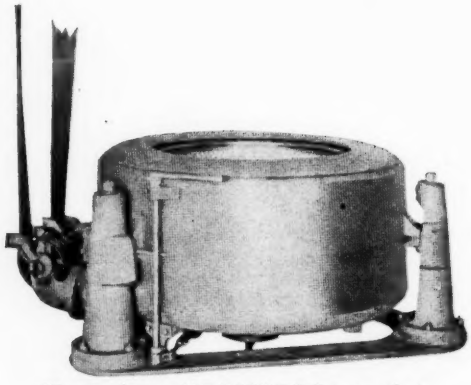

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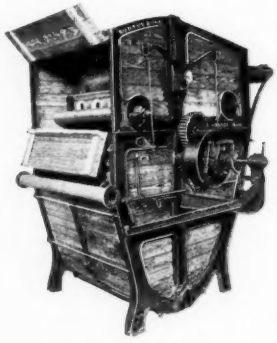

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"Circulated Everywhere Dyestuffs Are Used"

Devoted to the practical application of dyestuffs in all industries; especially to textile chemistry—the science and practice of scouring, bleaching, dyeing and finishing.

VOLUME XII NEW YORK, JANUARY 1, 1923 NUMBER 1

A History of the Chemistry of the More Important Natural Dyes

Effect of War on Position of Natural Dyestuffs—Early Dyes and Mordants—Principal Natural Dyes —Legal Ban on Logwood Under Elizabeth—Work of Chevreul—Work of Erdmann, Reim, Schultz and Meyer—Chemical Constitution of Hematoxylin and Brazilin—Investigations of Perkin the Elder

By EMIL LESSER, Ph.D.

American Dyewood Company, New York

THE object of this article is to present the development that has taken place in recent years in the chemistry and manufacture of natural dyestuffs. During the war, owing to the shortage of artificial dyestuffs, the natural dyestuffs again came into the limelight. In fact, if it had not been for the existence of the natural dyestuff industry in this country, many of the textile mills would have had to close down during the years 1915 to 1917. And those dyers who were, at first, reluctant to use dyewood products, were surprised at the results obtained, and they also found that the modern dyewood product, when properly used, could give superior and more economical results than the artificial dyestuffs.

Temporary Eclipse of the Natural Dyes

Years before the war, little was heard of the natural dyestuffs. They were looked upon as prehistoric. This was due to the rapid development of the coal-tar industry, for as soon as the manufacture of the artificial dyestuffs had been placed on a commercial basis, these manufacturers pushed the advertising of their products to the limit and the vast sums of money were spent in highly scientific propaganda. Dyehouses, technical colleges, etc., were flooded with literature and samples of their products, and so the natural dyestuffs were relegated to the background for the time being.

The art of dyeing must have begun with the employment of natural dyestuffs, so the history of the use of natural dyestuffs dates back to the earliest periods of civilization. One cannot say definitely where or by whom they were first used, but we have sufficient historical evidence. The Bible furnishes us with many examples, and so do the documents we possess relating to the history of the early Egyptians, and among such Asiatic peoples as had at any early date attained a high degree of civilization, especially the Hindoos and Chinese.

The process of dyeing adopted by the ancients must have been the staining of the fabric with an infusion of a vegetable material containing a tannin, for there are very few direct dyestuffs to be found in nature. Indeed, it was not until the discovery of the use of mordants that any real progress was made in the art of dyeing, and, as Bancroft says, this was one of the most important events in the history of dyeing.

Early Dyes and Mordants

The Hindoos are given the credit of being the first to use mordants and it has been proved that the Egyptians borrowed this knowledge from them, and that it then spread to Greece and Rome. The mordants at first employed were soluble minerals of alum and iron. With the introduction of mordanting it became possible to take advantage of the numerous mordant dyes which abound in nature.

The dyes used by the ancients were probably Madder, Woad, Indigo and Alkanet. According to tests made on samples of cloth taken from mummies of the early Egyptians, it seems that they were acquainted with the use of Indigo and Safflower.

Then there came a period in the world's history when the art of dyeing, as well as all arts and sciences, were lost for at least five centuries, due to wars and other conditions, and it does not seem to have been revived until the middle ages, the revival period of literature and science. The Jews were then the greatest dyers. In the fourteenth century a Florentine discovered the dyeing properties of Archil. In the sixteenth century Rossetti,

a Venetian, conceived such a passion for the art of dyeing that he devoted all his fortune to traveling and collecting the methods and means employed in dyeing in the various countries he visited. On his return home, he published an extensive work on the art of dyeing, which has been supposed to have contributed more than others to the improvements afterwards made in the art.

The discovery of America opened a new era in the progress of dyeing, for it gave the Old World the benefits of its valuable tinctorial treasures, such as Logwood, Cochineal, Annatto, Brazilwood and Fustic.

Principal Natural Dyes

The variety of dyestuffs to be found in nature is large. Those which have been of any commercial importance in modern times are comparatively few in number. They consist of Logwood, Brazilwood, Sandalwood, Barwood, Camwood, Madder, Cochineal, Annatto, Archil, Fustic, Quercitron Bark, Turmeric, Safflower, Persian Berries, Indigo, Woad, Cutch, Gambier, and a number of Indian dyes.

Since the discovery of artificial colors, a great number of the natural dyes have been replaced. Natural Indigo has practically been supplanted by the artificial, and the cultivation of Madder, which was carried on extensively in southern Europe, has been ruined by the discovery and manufacture of its coloring principle, Alizarine.

Logwood, Fustic, Brazilwood, Quercitron Bark, Persian Berries and Cutch have survived the competition of artificial colors.

Logwood, which is still considered one of the most valuable dyestuffs, was first imported into Europe by the Spaniards shortly after the discovery of America. The botanical name of the logwood tree is Haematoxylin Campechianum, which belongs to the family Caesalpinacae, and is a native of Mexico and Central America. It was introduced into Jamaica from Honduras in 1715 and was later planted in other parts of the West Indies. It is interesting to note that Honduras and Jamaica wood of to-day are totally different, both in physical and chemical properties. The Honduras wood has a round section, whereas the Jamaica wood is very irregular and full of grooves or "gutters." The dye from the Honduras wood, when used as a cotton dye, acts in a manner different from that of the Jamaica product. This is another instance of the effect of change of soil and climate on plant life. Logwood grows well in all soils, but it grows best and produces the best heart wood (which is the part of the tree used in the dyewood industry) in a moist, warm climate. There is no attempt made to cultivate it. It is a self-sown tree; in fact, it is only necessary to thin out the saplings in order to give promising trees advantage; otherwise a logwood plantation would become a veritable jungle. Land given up to the growth of logwood is useless for cattle raising purposes, as the logwood tree, in the course of its growth, makes the grass sour in its immediate vicinity. At certain seasons the logwood tree bears a small yellow flower (not unlike the honey locust) from which the bees extract honey. This honey, known as logwood honey, has a delicious flavor. At other seasons a gum exudes from the tree. When the tree is ready for the market (which usually takes from seven to twelve years), it is felled and trimmed of the bark and smaller branches by native labor and, in this condition, is shipped to the United States or Europe. The roots are also shipped, after being thoroughly cleaned. The wood, as received here, has a dark brown color, but internally is much lighter in shade.

Use of Logwood Prohibited Under Elizabeth

Strange to say, logwood was the subject of a British act of Parliament during the reign of Queen Elizabeth. The act is entitled "An Act for the abolishing of certeine deceitful stuffe used in the dyeing of clothes," and goes on to state that "whereas, there hath been brought from beyond the seas, a certeine kind of stuffe called logwood, alias blockwood, wherewith divers dyes, . . . etc.' and whereas, the clothes therewith dyed are not only solde and uttered to the great deceyte of the Queen's loving subjects, but beyond the seas, to the great discredit and sclaunder of the dyers of this realme: For reformation whereof, be it enacted by the Queen, our Soveraygne Ladie, that all such logwood in whoes handes soever found, shall be openly burned by the authoritie of the maior." Think of it! This act was passed in the twenty-third year of the Queen's reign and was re-enacted in the thirty-ninth, with the addition that the person so offending was liable to imprisonment and the pillory. More than a century elapsed before the real virtues of this dyewood were acknowledged, and there is no known natural dyestuff which is so universally used or so useful. Logwood was long used before anything was known of the coloring principles.

Readers of this article are all acquainted with the making of artificial colors by subjecting coal-tar products to operations like sulphonation, oxidation, and nitration, and combining the different resulting products with so-called intermediates. The synthesis and composition of these dyestuffs is therefore known and it is comparatively easy to make new combinations. The coloring matters which we meet in plants and trees are of a more complicated composition and the study of the real coloring matter has been the subject of many great chemists. As a rule, the color-giving matter of natural sources is not found as such in the plants, but is contained in what is chemically called "glucosides." We know that these bodies exist in all plants, but know little about their real composition because the glucosides change their nature sometimes very easily, and form other products which the chemist working on them gets from one field of operation to another. The usual method of changing a matter by nitration, sulphonation, etc., can seldom be used, as any strong action decomposes the glucosides. For this reason the chemists were obliged to employ

somewhat different methods to synthesize the natural coloring matters. The history of the most important natural color, namely, Logwood, furnishes the best illustration of the ways and means which have been employed for the synthesis of the natural colors.

Work of Chevreul on Logwood

The first serious attempt to study the nature of Logwood, chemically, was made by Chevreul. In 1810 Chevreul published, in the Annales, his treatise "Sur le bois de Campeche, et sur la nature de son principe colorant." He extracted the Logwood successively with water, alcohol, and hydrochloric acid and studied the various substances isolated. Finding the aqueous extract of the greatest interest for a more complete study, he subjected it again to the action of various solvents—water, alcohol and ether. From the alcoholic or ethereal extractions, by mixing with water and evaporating, he obtained crystals which he called Hematine, but later, to avoid confusion with the red coloring matter of the blood, he renamed Hematoxylin. Chevreul then made exhaustive studies as regards the physical and chemical properties of Hematoxylin, its reactions to acids, and a long list of metallic salts, but he made no attempt to determine the constitution of Hematoxylin. In his address to the Institute of France, Chevreul remarked, "When we consider the progress that chemistry has made in recent years, we are astonished at the small amount of knowledge in existence concerning the coloring matters of vegetables and at the little attention that has been paid to their study."

Contributions of Erdmann, Reim, Schultz and Meyer

No contemporary and no immediate successor continued Chevreul's work. For about thirty years there apparently was a blank. In 1840 Otto Erdmann picked up the thread of the investigation at the exact point where Chevreul had left it. Erdmann, with his pupils, worked on the subject at intervals for twenty years and considerably increased the exact knowledge concerning Hematoxylin. Erdmann improved on Chevreul's process for making pure Hematoxylin crystals, studied at length their crystallography, chemical properties and reactions, and proposed an empirical formula for Hematoxylin. He also first prepared, described and studied chemically the oxidized product of Hematoxylin, which he called Hematine. The latter is the real color-giving matter of Logwood.

The work of Erdmann was continued by Franz Reim, G. Schultz, and Richard Meyer. These men worked especially to find a chemical formula for Hematoxylin. They succeeded well and agreed on the figures $C_{16}H_{14}O_6$, which formula is used at the present day for Hematoxylin.

After having obtained from the glucoside of the Logwood tree the coloring principle, namely, Hematoxylin, the latter was subjected to the then known methods and it was found that nitric acid and chromic acid, even in the cold, destroyed Hematoxylin with violent effervescence. Sulphuric acid partly dissolves Hematoxylin, and by heating transforms it into a black mass, soluble in water with a brown color, but no trace of sulphonic acid could be obtained. Heated with caustic soda, Hematoxylin forms no ammonia, proving that it contains no nitrogen amido groups, but the resulting product could not be synthesized. Ammonia dissolves Hematoxylin with a red color, and, on standing, the Hematoxylin is oxidized to Hematine. The sensitiveness of Hematoxylin to the influence of ammonia makes it a most excellent reagent for qualitatively detecting traces of ammonia. Wildenstein (An. Chem. 1862, 830) made Hematoxylin reagent paper and claimed to detect thereby one part of ammonia in one million.

In their investigations on other natural colors besides Logwood, all the above-mentioned chemists, Chevreul included, found the essential coloring of the Redwood or Brazilwood, namely, Brazilin, to be strongly related to Hematoxylin:

Hematoxylin Formula	Brazilin Formula
$C_{16}H_{14}O_6$	$C_{16}H_{14}O_5$

The two have been proved to be essentially in kernel, Hematoxylin being the more complicated. Thus we see that the investigations, experiments and discussions concerning the constitution of Hematoxylin interlink completely with the study of the simpler and more easily reactible substance, Brazilin.

Perkin the Elder

The names figuring prominently in further investigations are Schalle and Dralle, Herzig of Vienna, Kostanecky of Berne, and last but nevertheless not least, Perkin the elder. All these men have done excellnt work, but all their investigations are not in entire harmony concerning the exact chemical constitution of Hematoxylin.

It would lead us too far to consider all the lines of attack of each investigator, hence the writer will confine himself to the experiments of Perkin. All the investigators ultimately came to the conclusion that Hematoxylin was of an alcoholic nature, but could be transformed by either bromation or methylation into a body which showed characteristics of a phenolic nature.

Whatever may ultimately be decided relative to the true constitutional formula of Hematoxylin—and this for synthetical work is of the utmost importance—to Perkin belongs the credit of first opening the way to a series of reactions that offer a possibility of transforming Hematoxylin into a new line of dyestuffs.

Chemical Principles

A few words relative to the chemical principles under-

fying the manufacture of azo dyestuffs (acid and direct cotton dye) will illuminate the discussion of these Perkin reactions. In the making of azo dyestuffs, the most important and prolific chemical process is the diazotizing and developing process. A certain base is treated with sodium nitrite and muriatic acid and is said thereby to be diazotized. This diazotized base can then be treated with another base or a coupling substance, and a development or condensation is said to take place, and the dyestuff is thus formed. Thus, if sulphanilic acid is diazotized and then treated with B. naphthol, Mandarin Orange is formed. According to the base first employed and the substance condensed with the diazotized base, different shades and different kinds of dyestuffs are formed. Thus, if for sulphanilic acid, as above, we substitute naphthionic acid, the result with B. naphthol is Fast Red A—a full medium red; if we use sulphanilic acid and substitute for B. naphthol (1:8) dioxy naphthalene monosulphonic acid (Sch. Amo Fucheine G), a handsome level-dyeing bluish red is obtained. All these products are acid dyestuffs. To make a direct cotton color, a doubly diazotizable base is taken and this is doubly diazotized and condensed. Thus tolidine doubly diazotized and doubly condensed with naphtionic acid yields Benzo Purpurine 4B. To make direct cotton blacks requires still a further diazotizing and condensation; these products are therefore called scientifically, tetrazo dyestuffs. The chemical complexity of these cotton colors explains, *en passant,* their relative lateness of appearance in the history of the development of synthetic dyestuffs.

Perkin in the course of his work on Hematoxylin made a substance which he found acted exactly like B. naphthol in condensing with diazotized bases to produce azo dyestuffs.

Objects of Perkin's Work

The general objectives of the experimental work were, first, to make the condensable Hematoxylin derivative; and secondly, to condense this derivative with the largest variety of diazotizable bases and to examine these products as to their commercial values.

The name of the condensable Hematoxylin derivative is oc anhydro tetra methyl hematoxylone. Starting with Hematoxlyin, the preparation of this derivative involves four steps. Hematoxylin is first methylated by treatment in methyl (wood) alcohol solution with caustic potash and di methyl sulphate. This gives tetra methyl hematoxylin. Tetra methyl hematoxylin is then oxidized by treatment with chromic acid (chrome and sulphuric acid) and tetra methyl hematoxylone is formed. By treatment of the hematoxylone with sodium acetate and acetic anhydride, the acetyl derivative, acetyl tetra methyl hematoxylone, is formed, and when this latter substance is dissolved in methyl alcohol and caustic potash the final derivative, the analog of B. naphthol, the oc anhydro tetra methyl hematoxylone is synthesized.

This oc anhydro tetra methyl hematoxylone we have made. The various steps in the synthesis have been studied carefully and with some obstacles overcome, have been well mastered. The passage from one substance to the next goes smoothly and the intermediate and final products obtained are of excellent purity.

Improvements over the Perkin process in some instances have been made. In the preparation of the tetra methyl hematoxylin, for instance, the time of methylation has been cut from forty-eight to twelve hours. In almost all instances where Perkin recrystallized his product our first crop of crystals were sufficiently pure, giving the requisite tests of the pure substances, to continue without recrystallization.

It may readily be seen that the chemists engaged in the business of natural dyestuffs have not been entirely idle in the further development of these products.

Perkin used the formation of colors made from a Hematoxylin derivative, similar to those made from coal tar, to prove his view of the constitution of Logwood. The writer is inclined to consider this view as correct, but as Pilate says, "Who knows the truth?"

Handy Graphics—I

Chart Your Tanks—Make Your Slide Rule Settings Permanent—Introducing Ratio Paper—True Pictures of Reactions

By CHARLES F. GOLDTHWAIT and JOHN E. HOFF

Chemists, the Clearflax Linen Looms, Inc.

Part One of a Series on Textile Chemical Uses of Ratio Paper and Logarithm Scales

WHO takes his pen in hand nowadays to write about graphic methods need not start with an excuse or an apology. A subject that has already furnished inspiration for a half-dozen recent good books and endless articles in the technical and business press *is* already established and accepted as a part of industry and commerce. Some of our large corporations already have their affairs pictured more plainly than in words or figures, and filed in the form of thousands of simple standardized charts, but there are still great opportunities for new uses and for improvements in technique. Our theme is ratio plotting or, if you are not afraid of its right name, it is the use of logarithmic paper and scales to present experimental results and business facts in a

simple, clear way, and to simplify certain kinds of computation.

Charting can easily become a hobby and be overdone, and of its multitude of forms, some will survive while many will not. Ratio charting, however, is being emphasized more and more in the literature and used more and more in practice as its merits are becoming known.

Easy Multiplying

Now look at *Fig.* 1, which is nothing more nor less than our old friend, the multiplication table, although we may not recognize him in this picture. The dotted lines are not for your name but to show how the chart works. You will notice, too, that it covers a number of intermediate decimals as well as the whole numbers from 1 to 12, and can be extended to higher numbers as well.

Start with 6×9. Scale from 6 on the left to the 45 deg. line marked 9, then drop vertically to the base line and find your answer, 54.

The next diagram works just like the first, only here we have a more practical case, a method of finding the contents of vertical cylindrical tanks filled to any height. Take the tank of diameter four feet six inches and assume that it has five feet of water in it. Scale from five feet (sixty inches) to the four-foot-six-inch line and read across to find the required volume, 592 gallons. Of course, it will also work backwards. Say we want to use 300 gallons of water in the seven-foot-six-inch tank. Run across from 300 gallons to the seven-foot-six-inch line and drop to the base, land at 11, the proper depth of water to be run in. This chart was made for certain tanks in regular use but it can be used for any number of others by putting in a 45 deg. line for each, and for square tanks as well as round.

Where the Logs Come in

It seems to be the custom of most writers who introduce the subject of ratio plotting to assume that their readers will be scared away at the mention of logarithms, so they hasten to explain that, while this is the basis of the work, you can use the charts perfectly well without understanding the underlying "theory." Perhaps that is true, but since logarithms are one of the simplest of mathematical devices and are introduced to us in elemen-

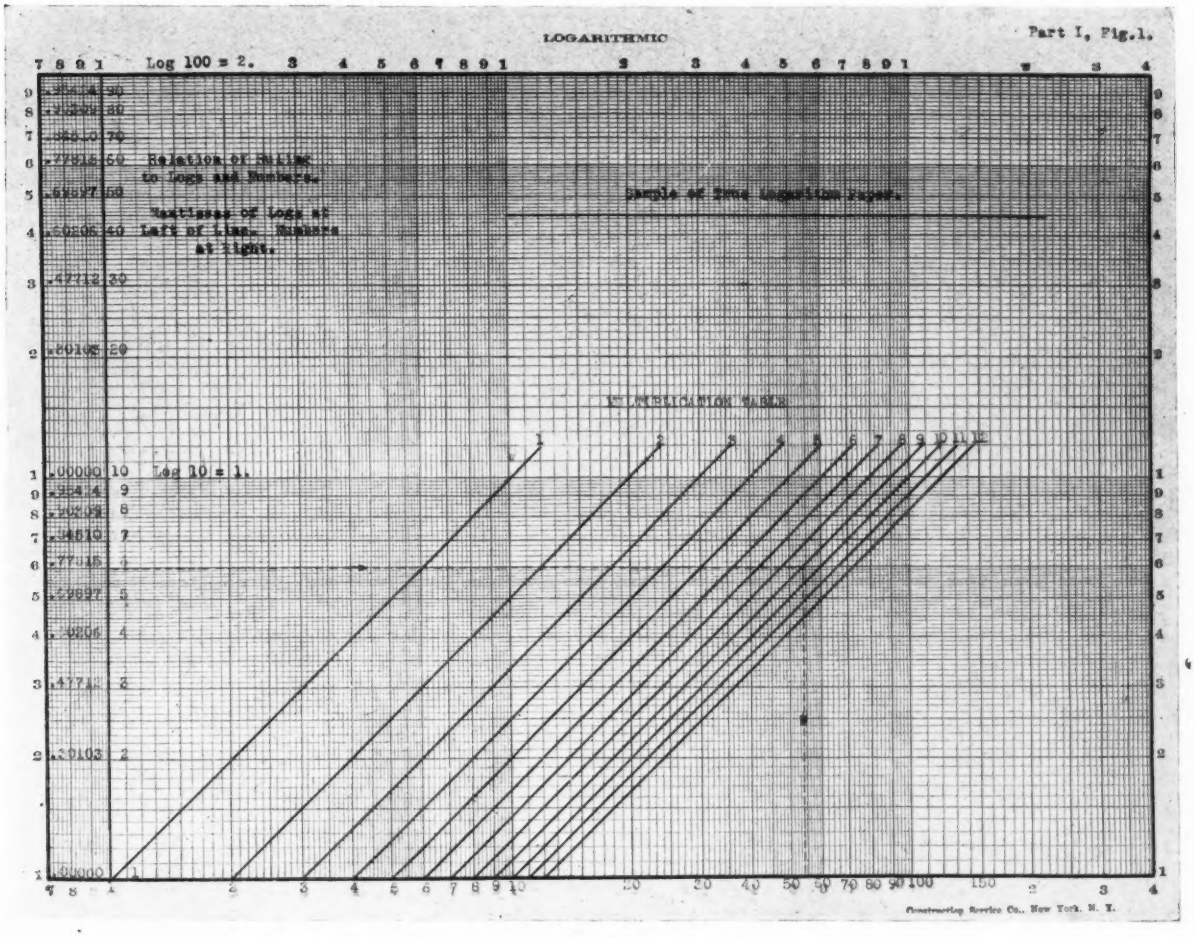

Fig. 1—*Multiplication Table*

tary algebra, it seems safe to take a little bolder attitude and at least mention them once in a while. The simpler style of business charts does not require any particular knowledge of logarithms, but special charts for calculations cannot be devised without understanding why they work.

One of the two usual types of logarithm paper was used in *Fig.* 1, with logarithmic rulings both ways, and we at once come to the main element of simplicity, the fact that, while the rulings are spaced logarithmically, they are marked with the ordinary numbers. The logarithms could be arranged in a scale with uniform divisions, but for convenience only those lines are actually drawn which correspond with the common numbers and their decimals. This gives the peculiar spacing. The whole matter is easiest seen by reference to the left-hand side of *Fig.* 1, where the numbers belonging to our chart proper have been extended to the top of the sheet and beside them have been written their logarithms. The numerical scale runs from 1 to 10 in the first cycle and 10 to 100 in the second; the third would be 100 to 1,000, and so on. The corresponding log scale is 0 to 1 and 1 to 2; 2 to 3 would come next if we had a third cycle. This amounts simply to the facts that the logarithm of 1 is 0; of 10 it is 1; of 100 it is 2; and of 1,000 it is 3. To multiply we merely add logarithms, and that is all we have done in our first two charts. Returning to *Fig.* 1, the 45 deg. line marked 9 starts at 9 on the base line and in so doing sets off a distance from the left equal to the logarithm of 9. Reading upward at the left to 6 indicates a vertical distance equal to the logarithm of the other number entering into our product and following the dotted line transfers this distance to the base line and adds it to the first "log," so we arrive at the sum of the two logarithms but on our scale it reads directly as the desired product, 54.

The idea in the second chart is just the same. The volume of a tank filled to given height can be expressed as the product of a constant factor (its cross-section, including a gallon or other conversion factor) into a variable its height. The factor is worked out and since it is a constant it gives a starting point for the 45 deg. line which happens to be measured upward this time to better accommodate the chart to the paper. Read any given height on the bottom line, scale upward and then across and read the volume at the left. You have added the logarithm of the height to that of the constant factor and obtained that of the volume, which can be read di-

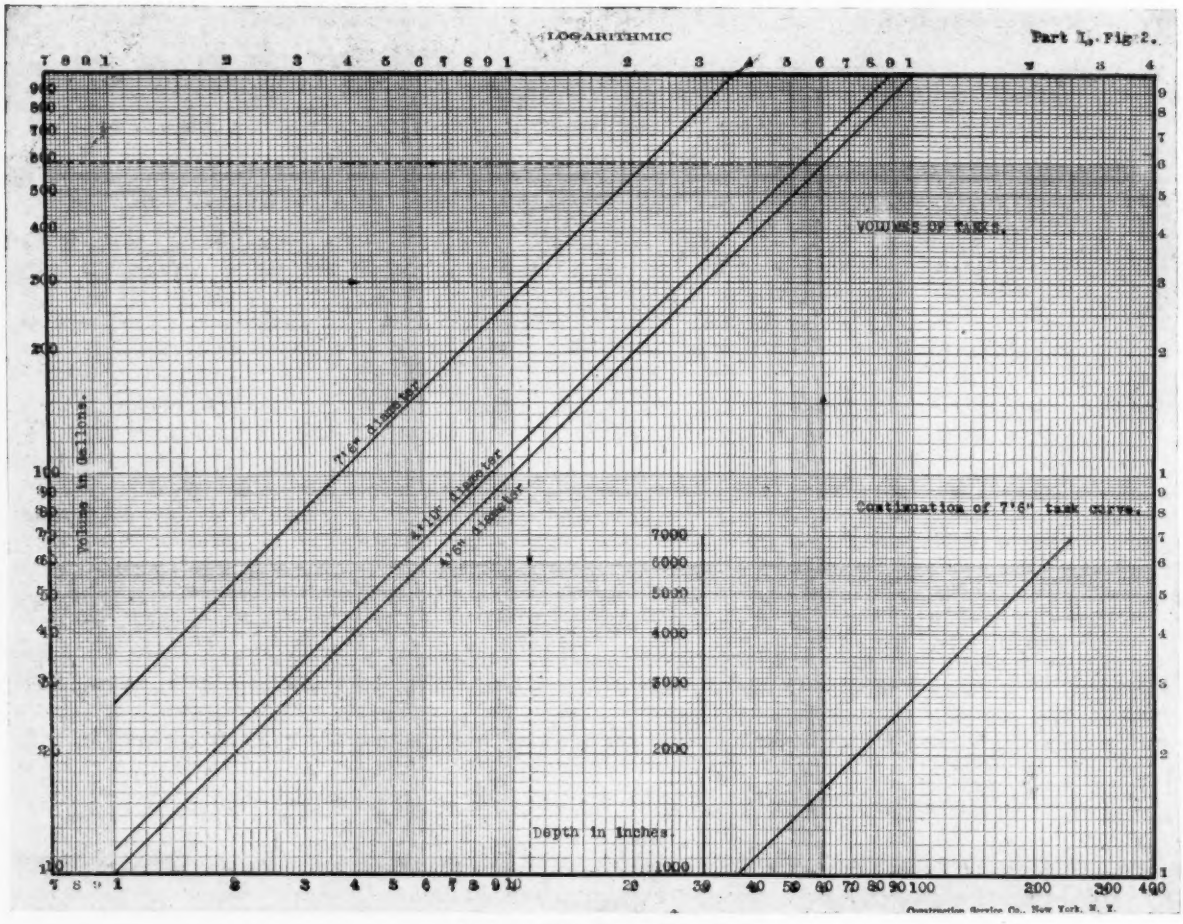

FIG. 2—*Volumes of Tanks*

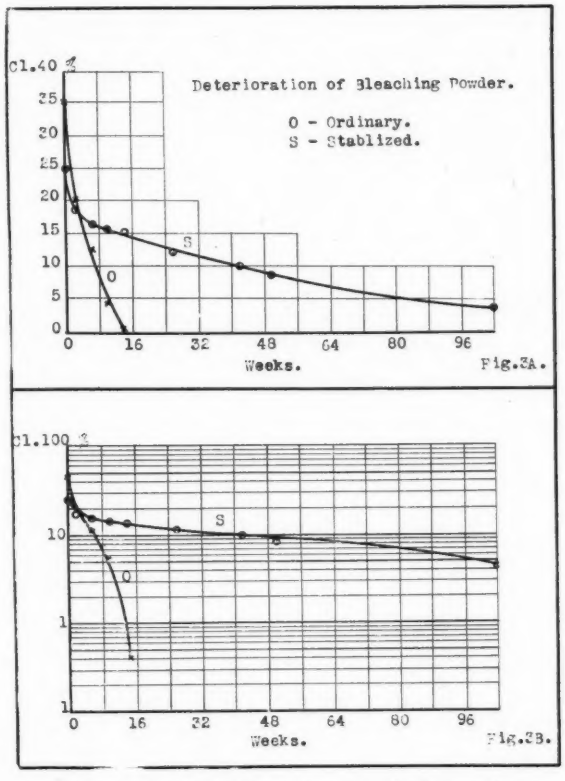

FIG. 3—*Graphic View of a Chemical Reaction*

rectly as the corresponding number, the volume in gallons

The multiplication table is too simple to warrant the construction of a chart except to illustrate a principle. For tanks which are frequently used filled to various heights we can often save time over direct calculation or the preparation of tables.

The accuracy depends much on the paper used. It looks as though readings toward the upper part of the sheet for tank volumes would be less dependable than those near the bottom. Actually the percentage error is the same at all points, a fact that can be easily verified. for finer readings it is possible to draw only the more active sections of the charts and to put them on paper that measures 10 inches to the cycle.

The writers have also used the same principle for routine work where constants are multiplied by various values. Numerous little charts can be drawn on a single sheet and each really amounts to a permanent slide rule setting. Like a slide rule, if you run off the sheet at the right, come back on again at the left and go right along. Division can be effected by working backwards.

"Double log" can also be used for more complicated calculations in costs and mechanical designing, for plotting various sorts of experimental results and for the derivation of mathematical formulas, especially those containing powers and roots. Experimental values frequently fall into straight line "curves" on this paper when they are of some other shape on ordinary paper, and formulas can be easily derived from such straight lines. Conversely, equations often give straight lines and specific values are readily found. Interpolations and extensions of "curves" which are straight can be made easily

For further reading, possibly Haskell[1] contains the most information of any one source.

Our first type of paper finds little use in business, although convenient for many technical matters. Of more universal interest is semi-logarithmic or the true ratio paper whose business uses are rapidly becoming better appreciated. We will start, however, with a chemical illustration.

An article published in the Journal of the Society of Chemical Industry[3] gave the following figures showing the rates of decomposition of ordinary and "stabilized" bleaching powder, the latter consisting of regular good bleach mixed with 20 per cent of dry quicklime:

Loss of Strength of Bleaching Powder

	Per Cent Chlorine in Bleach	
	Ordinary	Stabilized
Analysis in England before shipping.	35.00	25.00
Analysis on arrival in India.....	20.04	18.40
Analysis after storing 6 weeks....	12.52	16.56
Analysis after storing 10 weeks....	4.68	15.90
Analysis after storing 14 weeks....	0.42	15.05
Analysis after storing 26 weeks....	....	12.08
Analysis after storing 42 weeks....	....	10.00
Analysis after storing 52 weeks....	....	8.50
Analysis after storing 104 weeks....	....	3.48

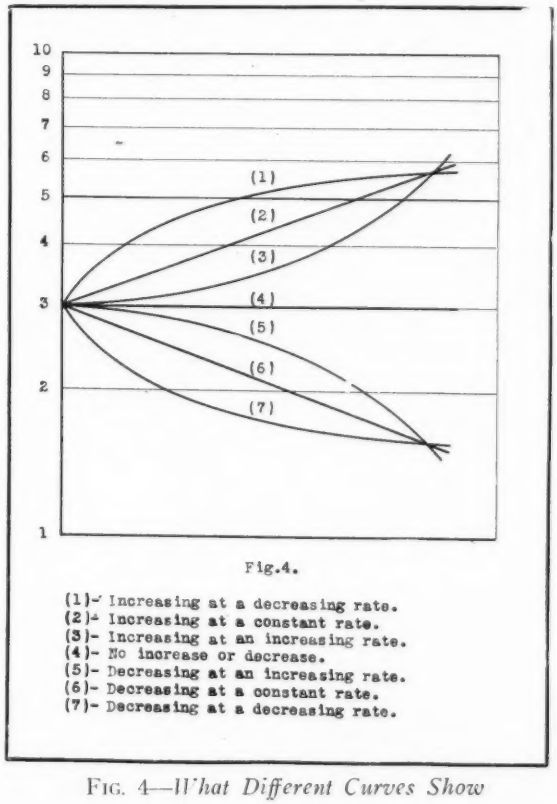

FIG. 4—*What Different Curves Show*

In *Fig.* 3 the upper chart is an ordinary plot from the data in the Table, made by the present writers to show the approximate course of the reaction, while the lower contains the same data on ratio paper. A striking difference is at once evident. Instead of the reaction gradually growing slower as seems to be indicated by the curves in A it is gradually growing faster and faster, as shown by the increasing downward curvatures in B. To be sure, the amount of bleach undergoing change is becoming less and less and the products of the reaction are accumulating less rapidly, but the actual rate of change with reference to the amount of undecomposed bleach on hand at any time is increasing. Although the original authors called attention to this point it is not easily seen from the table or *Fig* 3A, plotted on ordinary cross-section paper. This relation *does* show in *Fig.* 3B because with ratio paper an increase in rate is automatically shown by an increase in the slope of the curve.

The reasons for this will be seen in Part II, where other uses of ratio paper will be taken up in greater detail.

Such stabilized bleach is obviously not a necessity and would not be convenient for common use but it has a value in hot climates. Ordinary bleach, not carefully stored, will undergo the same sort of decomposition in a hot, damp warehouse. The lime-bleach mixture may be of practical interest where small amounts have to be kept under unfavorable conditions for long periods of time and would seem much safer for the grocery store packages or wherever chloride of lime is depended upon for its disinfecting value.

Apart from any specific interest attaching to the bleach, the figures were borrowed as the most convenient example of this principle and it is believed that many reactions can be plotted in this way to bring out obscure points and show relations more plainly.

The possibilities are shown by *Fig.* 4, where each is marked according to its significance[2]. Such plotting will find numerous applications in addition to registering the effects of chemical change.

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Dyeing Woolen Yarn for Knitted Wear

Dyer Should Know Requirements—Fastness to Light Requirements—Alizarines—Fast and Bright Shades—Some Popular Shades—Olives and Browns—Reds—Dyeing Black—Apparatus Dyeing—Necessity of Softened Water

By E. SEKINGER

OF late years the demand for knitted outer garments has increased considerably. The greater interest developed in winter sports has created a demand for outer knitted garments which has given the manufacturer considerable work to keep abreast of the needs. The tendency on the part of all to turn to knitted garments has been in part due to their practicability, the ease with which the muscles can play, the freedom of movement—all have helped to make this material one of the most popular for winter sports.

The fashion of knitted wear subjects the dye works to particularly high demands, as for this purpose, in particular, vivid, bright—yes, loud—shades are demanded. This leads me to give further details in the following paragraphs in regard to the important field enjoyed by this branch of manufacture, the dyeing of woolen yarn for knitted apparel.

Dyer Should Know Requirements

It is the duty of the dyer to dye material properly, but this does not mean that he must dye it as fast as possible to washing, light, wear, rubbing, etc. For one thing, with many colors, particularly the bright ones, it is impossible to meet these requirements, and, for another thing, special arrangements and more expensive dyes are necessary for fast dyeing, so the question of expense becomes an important factor. For economic reasons it is therefore very essential that the dyeing be made as fast to certain requirements according to the use to which it is to be put. The dyer must know, when determining the manner of dyeing and the selection of the dyes to be used:

1. To what processes of manufacture the dyed material has still to be subjected and what influence they will have on the dyeing.

2. To what use the finished goods are to be put and the resultant influence on the color, and also how any necessary cleaning can be done.

In the case of dyed woolen yarn for knitted clothes, during the manufacturing processes of knitting, steaming, fulling, ironing, following the process of dyeing, the influence on the dyeing is so slight—practically nil—that the dyer can immediately resort to the simplest manner of dyeing—that is, with the acid dyes. The yarn dyed with these colors can be subjected without any injury to the shade to the processes that follow.

The conditions in the case of yarns for woven cloth are entirely different: they must be dyed with abso-

(*Continued on page* 29.)

Proceedings of the American Association of Textile Chemists and Colorists

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L. C. Lewis, Secretary, 95 Madison Avenue, New York City.

Philadelphia Section—
Robert E. Rose, Chairman, E. I. du Pont de Nemours & Co., Wilmington, Del
Elmert C. Bertolet, Secretary, Philadelphia Textile School, Philadelphia, Pa

Second Annual Meeting

Held at Hotel Pennsylvania, New York City, Saturday, December 2, 1922

MORNING SESSION

The Second Annual Meeting of the American Association of Textile Chemists and Colorists convened at 10.15 o'clock at the Hotel Pennsylvania, New York City, President Louis A. Olney presiding.

President Olney—When the Council originally made plans for our meeting they did not have a morning session scheduled, but the responses to our questionnaire came in so well we soon found we were really going to have more than enough for an all-day session, so it will be necessary to live up to our schedule in order to cover our program. While we would like to have long and full discussions of the papers, to start with we must limit the discussions to some extent. If we find that we can get through our morning program earlier than we anticipated, we will then give you more time to discuss any or all of the papers.

The first paper on the program is entitled "Properties of Hydrosulphites and Sulphoxalates," by Dr. Charles H. Hollander. Dr. Hollander! (Applause.)

Dr. Charles H. Hollander—Mr. Chairman and Gentlemen: I don't know that I deserve the honor of reading the first paper this morning. In this paper, I do not pretend to give you anything startlingly new on the subject, but there is so little known of these very interesting compounds in the chemical literature that I thought it might be of some interest to point out some chemical properties of these useful compounds.

. . . Dr. Hollander then presented his prepared paper as follows:

SOME PROPERTIES OF COMMERCIAL HYDROSULPHITES AND SULPHOXYLATES

By DR. CHARLES S. HOLLANDER

Rohm & Haas Company, Philadelphia, Pa.

Sodium hydrosulphite, $Na_2S_2O_4$. The commercial product is a white or grayish white granular powder that will run freely somewhat like sea sand. It may be analyzed by any of the methods published in the literature, but for ease and speed of operation and exactness we recommend the method we have published in the AMERICAN DYESTUFF REPORTER of October 11, 1920. The constitutional formula of this compound has been established to be:

$$O\diagup\!\!\diagdown SO_2Na$$
$$\qquad\diagdown\!\!\diagup SO\,Na$$

Dissolved in water it forms the hydrate $Na_2S_2O_4 + 2H_2O$, which crystallizes in needle-shaped crystals and is somewhat less scluble than the anhydrous product. This

hydrate is not stable and therefore not a commercial article. The hydrosulphite is very easily oxidized by the oxygen of the air, especially if this oxidation is catalyzed by the presence of traces of moisture, which are always present. In solution it very rapidly oxidizes according to the formula $Na_2S_2O_4 + O = Na_2S_2O_5$. While the hydrosulphite itself reacts neutral, its oxidation product bisulphite, or rather metabisulphite, reacts acid, and the acidity of the oxidation product accelerates the rate of decomposition by producing the free hyposulphurous acid, which is far less stable than its neutral salts. While this decomposition through atmospheric oxidation is the most important phase, the process of auto-oxidation is also very appreciable, even in the complete absence of oxygen, both in solution as well as in the solid form, according to the formula $2Na_2S_2O_4 = Na_2S_2O_3 + Na_2S_2O_5$. The presence of acids accelerates this auto-oxidation and reduction, and in order to make the solution in the absence of air more stable a large amount of alkali should be added, which acts as a retarder for this auto-oxidation, although it will always take place in any solution to an appreciable amount if kept for more than a few hours, even in the complete absence of oxygen.

Solutions of sodium hydrosulphite undergo decomposition by atmospheric oxidation and also auto-oxidation and reduction in the absence of air a great deal more readily the higher the temperature is raised. The decomposition by heat is practically complete after boiling up the solution, and at lower temperatures the decomposition will be complete after a short interval of minutes. In short, it is only possible to preserve sodium hydrosulphite by keeping it cool, absolutely dry and by having present some alkaline stabilizer.

The hydrosulphite of soda is the only hydrosulphite that has gained commercial importance, while others, like the potassium, calcium, magnesium and zinc hydrosulphites, are also well known to science.

The largest use for sodium hydrosulphite is as a reducing agent in the indigo vat and for the application of vat dyes and sulphur dyes; besides this it is used in increasing amounts in the bleaching of straw and other vegetable fibers, sugar, molasses, soap, and for the manufacture of certain dyes, salvarsan or arsphenamine and many other smaller purposes. It is an inexpensive and efficient oxygen absorption reagent, and may very effectively be used in gas analysis for the removal of oxygen.

If a solution of sodium hydrosulphite be acidified, a strong brownish yellow color appears, which is the color of the solution of the free hyposulphurous acid, a very unstable substance, which soon decomposes into free sulphur, sulphur dioxide and water $2H_2S_2O_4 = 2H_2O + S + 3SO_2$.

If the salts of this acid, for instance sodium hydrosulphite, are treated with two molecules of aqueous formaldehyde, the molecule will split into two compounds. One-half will react with formaldehyde to form sodium bisulphite formaldehyde, and the other half will form sodium sulphoxylate formaldehyde, according to the formula:

$$O\begin{matrix}\diagup SO_2NaH \\ \diagdown SO\ NaOH\end{matrix} + 2CH_2O = \begin{matrix}SO_3HNa\,.\,CH_2O \\ + \\ SO_2HNa\,.\,CH_2O\end{matrix}$$

This latter part, the sodium sulphoxylate formaldehyde, is of great commercial importance and may be distinguished from the formaldehyde bisulphite compound by its solubility in alcohol.

Sodium sulphoxylate formaldehyde has the formula $NaH\,SO_2CH_2O + 2H_2O$. It crystallizes very beautifully in large glass clear crystals of the rhombic system, and these crystals are stable for a short time only. However, it is quite possible to prepare these large crystals in a dry state and use them for the standardization of copper ammonium sulphate solutions, if used immediately. This pure compound cannot be used commercially, since it breaks down too easily, forming compounds of sulphureted formaldehyde, bisulphite formaldehyde and sulphurous acid. The sulphureted compounds of formaldehyde are the cause of the garlic-like smell of decomposed sodium sulphoxylate formaldehyde. The commercial product always contains sodium bisulphite formaldehyde and some sodium carbonate as stabilizers. It is sold in the form of white or grayish white broken lumps of a microcrystalline nature. It may be analyzed by a similar method to that for sodium hydrosulphite. Unlike the sodium hydrosulphite, the sulphoxylate formaldehyde compounds are quite stable under ordinary circumstances to the oxidizing influence of the air, and also to heat, since they do not start to decompose rapidly until raised to the temperature of boiling water, but they should be protected against moisture to prevent gradual decomposition.

A solution of sodium sulphoxylate formaldehyde is fairly stable at the boiling temperature, but breaks down more rapidly in the presence of substances that will give off oxygen. If acidified, the formaldehyde sulphoxylic acid is liberated, and this acid is fairly stable in water solution for short periods at temperatures not exceeding 120 deg. Fahr. It will slowly break down at temperatures above this and form sulphur, according to the formula: $2H_2SO_2 + CH_2O = S + H_2SO_3\,.\,CH_2O + H_2O + CH_2O$. There is also a side reaction which generates some hydrogen sulphide and sulphureted formaldehyde. The isolation of the free formaldehyde sulphoxylic acid has not yet been accomplished.

Sodium sulphoxylate formaldehyde finds its chief uses in the preparation of reducing pastes for discharge printing and for stripping, and in a minor degree in bleaching operations with soaps, oils and raw cotton at elevated

temperatures; also in the manufacture of neo arsphenamine.

Zinc sulphoxylate formaldehyde has the formula $Zn—(H\,SO_2CH_2O_2)_2+2H_2O$ and is very easily soluble in water. It is a white crystalline powder. It is even more resistant to heat and oxidation than the sodium salt, and finds its chief application in stripping operations where it shows a remarkable reducing power, due not only to its great concentration (it is about 20 per cent stronger than the sodium salt), but also to its greater resistance to the heat, thus insuring a longer continued stripping action. On union goods, it may be used alone in a boiling solution and on wool and silk stripping in an acid solution. It is also used to a smaller extent in the bleaching of glue, sugar and molasses.

Basic zinc sulphoxylate formaldehyde, $ZnOH—H\,SO_2CH_2O$, is a white or grayish white powder that is almost insoluble in water, but is used for stripping in conjunction with mineral or organic acids, according to the nature of the goods to be stripped. The regular commercial product leaves a slight residue on dissolving in acid. On very fine fabrics a purified product that dissolves without any residue in acid should be used. This basic salt, if equivalent, acts exactly like the soluble normal zinc sulphoxylate formaldehyde compound, described above.

Sodium sulphoxylate acetaldehyde has been recently recommended for discharging of Naphthylamine, Claret, Toluyene, Orange R and others.

It is analogous to the formaldehyde compound with the difference that it breaks down considerably easier and thus causes a better reduction of difficultly reducible dyes. If any demand for this compound should develop, it could be produced in a short time.

President Olney—We all know that in recent years hydrosulphites and related compounds have become so important that there is scarcely a branch of textile coloring to which they are not applicable, and I do not believe we can find anywhere as much information about these hydrosulphites brought together in a small space as Dr. Hollander has given to us this morning.

We have about fifteen minutes for discussion of this paper. Because we have so little time, however, doesn't mean we wish to curtail the discussion so that there will be none at all.

A. E. Hirst—I would like to ask Dr. Hollander what is the most generally accepted method of titrating these compounds.

Dr. Hollander—Well, I don't know whether any method has been officially accepted by anyone. We have persistently recommended the copper ammonium sulphite titration method because it is far easier to perform than any other method that we know of. But that is not the only method that will give correct results. However, as I say, it is the speediest method and gives results that are accurate within half a per cent, which is plenty accurate enough for compounds that decompose while you are looking at them. There is no sense in analyzing a compound like sodium hydrosulphite to a tenth of a per cent. You can't get two samples alike no matter how carefully you titrate, so within one-half of a per cent is sufficiently accurate.

The method, as I mentioned, is given in the October, 1920, number of the AMERICAN DYESTUFF REPORTER. Of course, if necessary I will give more information.

W. H. Wingate—Is it possible to get as heavy shades by using the hydrosulphite with the sulphur dyes as you do with sulphide of sodium?

Dr. Hollander—That is an entirely new field; but we have obtained, on the selection of some sulphur dyes, almost any shade that you could get with sodium sulphide. You can't use every sulphur dye with good results, but quite a number of them will give very good results with hydrosulphite instead of sodium sulphide, and quite as heavy.

The shade is, approximately speaking, the same; sometimes it is a little clearer, more brilliant. It enables you, of course, to apply vat dyes and sulphur dyes in mixture by that process, and you would need about one-fifth to one-tenth the amount of sodium sulphide that is ordinarily used.

Mr. Beattie—I should like to ask Dr. Hollander if there has been any experimental work done as to the effect this sodium sulphoxalate formaldehyde has upon the various fibers as compared with other stripping agents. I have not used this material myself, except in an experimental way, and I just wondered if there had been any work done along these lines.

Dr. Hollander—If the sulphoxalates are used by themselves—it depends on whether you have a sulphoxalate that would be naturally more neutral than the others. For instance, a sodium sulphoxalate formaldehyde is slightly alkaline to preserve it from too early decomposition, and in that case, of course, we would only recommend it for use on cotton. Cotton can be boiled fairly easily and sodium sulphoxalate formaldehyde is quite suitable there. But for the ordinary stripping, the bulk of the stripping is done on wool for shoddy manufacture, and that is always in slightly acid solution, either acetic acid or sulphuric acid, and it does not seem to harm the fiber in any way, because you are dealing with very low concentration of acid, far lower than you need for carbonizing. So your wool is surely not affected.

W. S. Williams—I should like to ask Dr. Hollander which form of hydrosulphite he recommends.

Dr. Hollander—Sodium hydrosulphite.

Mr. Lawton—I should like to hear the principal ob-

jections to the iodine method of titration. We use it at the United States Finishing Company almost entirely and we think we have got a method of getting the result in a quicker and easier and more satisfactory way than the copper method.

Dr. Hollander—If you take the proper precautions, there is no prejudice at all against it. But if you have any compound that is either short of alkali or short of formaldehyde, you will simply titrate some of your bisulphite with the iodine and get values that are too high.

Mr. Lawton—We add formaldehyde first before titrating.

Dr. Hollander—It is perfectly correct then.

William K. Robbins—What are the comparative values of caustic and carbonate as stabilizers for the hydrosulphites?

Dr. Hollander—That does not seem to make much difference. Anything that is alkaline in solution will act as a stabilizer. Very often caustic is taken, and sometimes carbonate. It doesn't seem to make much difference which is used.

William D. Livermore—At the risk of asking the gentleman to repeat something I apparently missed, I would like to know what the actual use of the hydrosulphite is in dyeing cotton goods, in place of the ordinary sulphide.

Dr. Hollander—In some instances that we have noticed—of course, we haven't been able to try all the sulphur dyes on the market; in fact, we have only tried a few—we get a distinctly clearer and better shade. It seems that the hydrosulphite will only reduce part of the sulphur dyes, and it seems in some cases the most invaluable part is not reduced, so that the impurities that are in the sulphur dyes are not made soluble and hence do not go on the fiber.

In some instances you have the great advantage of being able to dye vat dyes and sulphur dyes together in hydrosulphite.

Hugh Christison—I would like to ask Dr. Hollander if this hydrosulphite method of sulphur dyeing would make the sulphur dyes applicable to union goods.

Dr. Hollander—That is just the point I wanted to add. It is quite possible to dye silk, for instance, with sulphur dyes if you use sodium hydrosulphite instead of sodium sulphide. We have had quite interesting results in that connection, and very brilliant shades.

Mr. Christison—In the case of wool being present, could you use the sodium hydrosulphite and ammonia, and dye the cotton fairly well with the sulphur colors, and then perhaps dye the wool with an acid color afterwards?

Dr. Hollander—I haven't tried that exactly. We have dyed some union goods. You will find that the wool, under those circumstances, will take up the color as well as the cotton, but not exactly the same shade. That may be in some cases an advantage and in others a disadvantage. But we have not tried to apply an acid dye to the wool afterwards separately.

Mr. Christison—In using the hydrosulphite method with sulphur colors do you have to adopt any precautions to prevent reoxidation of the dye bath?

Dr. Hollander—We did not find that it was very necessary to protect it from reoxidation. Of course, there will always be some reoxidation and that has to be counteracted by adding a little more hydrosulphite. Very often a little scum is formed on top, the same as on indigo, of course, and that would protect the bath anyway. But we haven't found any inherent difficulties there.

Mr. Christison—What temperature do you recommend for dyeing the sulphur colors with hydrosulphite?

Dr. Hollander—You can get it up to 180 or 190 degrees if you want to, but I think most of the time a lower temperature is quite sufficient. I have no special case in mind, but I may be able to help you out if you wish me to in this connection.

President Olney—This discussion is very interesting and important, but we have run over our time limit on this particular paper; if there is time later we will come back to this subject.

The next paper is entitled "Why Silk Dyers Should Insist Upon a Report on the Quality of Raw Silk," by L. C. Lewis. Mr. Lewis!

. . . Mr. Lewis presented his prepared paper as follows:

WHY SILK DYERS SHOULD INSIST ON A REPORT ON THE QUALITY OF RAW SILK

By L. C. Lewis
Lewis Testing Company, New York

Raw silk is the most valuable material used in the manufacture of textiles, yet it is surprising how few manufacturers make tests of this same material for which they spend $300,000,000 each year. The average manufacturer merely picks up his telephone receiver, calls up a raw silk importer and, after discussing prices for a while, orders his raw silk. In doing so he depends entirely upon the importer to deliver to him the grade of silk which he pays for, and this is exactly what he gets, for when he beats the importer down 10 or 15 cents per pound he should not expect the grade ordered.

The silk manufacturer sends the silk to the throwster and has it thrown into two, or three thread organ, or three, four, five, six, seven, eight, nine, ten or twelve thread tram. The rereeled Japanese silk runs well on the winding, especially if the silk is soaked, which removes the hard gums which cause most of the breaks in the throwing plant during winding. The very fine ends all break during the winding, and when the silk comes to the spinning and doubling processes it is

raised one or two qualities and gives the throwster very little trouble.

The silk is then sent to the dyer in skeins to be dyed, and the dyer, not knowing whether the silk is a double extra or a number 1, with a high cohesion or low cohesion, puts it through his regular boil-off, weighting and dyeing processes. When the silk is dried and finished, the dyer in many cases finds the silk hairy or occasionally lousy; and he does not know whether the fault was in his dyeing or in the raw silk. If he had had a comprehensive report from a reliable testing company he would, on the other hand, be able to tell very soon whether or not the fault was his. Raw silk with a high cohesion will boil off and dye without showing any signs of hairiness, while raw silk with a low cohesion will be hairy after these operations.

If the dyer does not report this lousy condition to the manufacturer the latter discovers it when he winds and weaves the silk. First of all, he blames the dyer for this hairy or lousy silk; but if he had had in his possession a trustworthy report on his raw stock, he would know at once whom to blame.

American silk manufacturers should have all of their silk tested by a reliable laboratory, reject the silk that is not up to the standard paid for, and send a copy of the report to the dyer. As long as the silk importers can sell a No. 1 silk as double extra, and so get 50 cents more per pound, which on a five-bale lot means $325 extra, they will do it.

Subjoined is a quotation from the Textile American under the heading "Standards of Quality," which appears to be pertinent.

"Probably at no other time in the history of the silk industry has the quality of a fabric been of greater importance. Starting at the time of the buyer's strike in 1920, the preference of the consumer for the products of mills which have established a quality for their fabrics has become increasingly evident.

"A paragraph in one of the recent numbers of Textile World emphasizes this point so clearly that the liberty is taken of quoting it:

" 'One of these days manufacturers and merchants are going to wake up to the fact that the buyer's strike against high prices is not to be broken by the offering of inferior merchandise.'

"Some of the most noteworthy successes in a generally unsuccessful season have been in mills with unusually high-grade fabrics, while in other instances firms whose prices seem to be within the ideas of the purchasor have had hard sledding."

President Olney—Is there any discussion of this paper? I think we realize, in the case of silk, the importance of accurate knowledge of the fiber, on account of its extremely high price. With cotton, we will say, at an average of 20 cents a pound, the loss of a few hundred pounds doesn't matter so much; but with silk at $7 a pound, or higher, there would be a considerable monetary loss, even with a small quantity. I think therefore Mr. Lewis' paper should appeal to silk dyers in many ways.

If there are no questions, we will pass on to the next paper, entitled "Application of Vat Colors in Calico Printing," by Fred Whittaker. I might say that Mr. Whittaker has come from Canada to present this paper. I received a letter two or three days ago saying he would be unable to come, but when he saw our attractive printed program he changed his mind and came along. Mr. Whittaker! (Applause.)

Fred Whittaker—Mr. Chairman and Gentlemen: My principal object in presenting this paper is to bring before your notice a new method of applying the vat colors in calico printing, which has been used successfully now for the past six years; and after such a successful test, I think it is quite time now that we publish it.

. . . Mr. Whittaker then presented his paper, as follows:

THE APPLICATION OF VAT COLORS IN CALICO PRINTING

Principal Styles — Classification of Vat Colors — Factors to Be Considered—Methods of Applying Color—Powder Vat Colors—Recipes and Examples—New Silicate of Soda Caustic Soda Substitute for Carbonate of Potash—Various Assistants —Notes on Aging—Drying—Washing Off and Aftertreatment—Remarks

By F. Whittaker

Chemist, Dominion Textile Company, Ltd., Magog, Que.

Principal Styles

The ever-increasing demand of the public for Fast Color Prints has, within recent years, necessitated the manufacturer adopting the Vat Colors for certain styles, such as Shirtings, Linings, Dress Goods, Handkerchiefs, etc.

Classification of Vat Colors

These Vat Colors are comprised of three series of Dyestuffs, namely, the *Anthraquinanoid Series*—examples: Indanthrene, Cibanone Colors, etc.; the *Indigoid Series*—examples: Helindone, Thio Indigo, Ciba, Durindone, etc.; and also, the *Sulphurized Anthracene and Indiphenol Dyestuffs*—example: Hydron Blues, and certain colors as Indanthrene Olive, Cibanone Olive, Cibanone Orange, Blue 3G, etc.

Factors to Be Considered

In the application of these colors one cannot generalize with any degree of success, as in the case of the

Basic and Chrome Colors where one receipt is found in common practice for each respective series. The Vat Colors, if they are to be applied successfully, require to be studied individually, for the reason that the high cost of this Fast Range of Colors makes it imperative that the maximum tinctorial value must be obtained in order to be able to produce Guaranteed Fast Goods at a minimum and marketable price. It is also essential in order to obtain regular results or otherwise expressed perfect fixation of the Dyestuff.

Experience in the application of a considerable number of these Vat Colors in practice showed it was essential to have at least six modified formulae for the preparation of the various Colors in order to obtain maximum fixation, with local steaming facilities available.

Method of Applying Color

The application of Vat Colors is brought about by what is known as a reduction process, which involves the transformation of the Insoluble Vat Color into the Soluble Form, in the latter form it is readily absorbed by the fiber in the presence of an Alkali. The material is then subjected to a washing process, and this brings about the oxidation of the coloring matter, reconverting it back to the insoluble form, and, as such, they prove so resistant to the action of light and laundry treatment.

The reducing agents principally employed are known as Hydrosulphite and Rongalite C. (Formaldehyde and Sulphoxalate of Soda), but occasionally use is made of Glucose, for with certain colors it offers slight advantage.

Before giving any description of the various modifications of the "Hydrosulphite Process" it is worthy of note that within recent years much progress has been made in the application of the Powder Vat Colors for Printing. This effects considerable saving in freight, and obviates such troubles as occur from climatic conditions, etc.

The Powder Vat Colors

The modern Calico Printer looks upon the milling of color as an operation of the past. Colors of the Pigment Type, such as Ultramarine, Lampblack, etc., are not to be found in general practice to-day. Therefore, if the application of the Vat Colors in Powder form was dependent upon having to be milled they would not meet with any marked degree of favor. Happily, however, it is within our means to apply these Vat Color Powders by recipes which obviate the long, tedious process of milling. In favoring the use of Vat Colors in Powder form the writer can state with authority of their commercial success in this direction.

Recipes and Examples

The six formulae previously cited consist of:

1. Potassium Carbonate Rongalite Process.
2. Eight degree Twaddell Caustic Soda Hydrosulphite, Rongalite C. Process.
3. Forty to forty-five degree Twaddell Caustic Soda, Rongalite C. Process.
4. Vatted in weak Caustic Soda and Hydrosulphite, and printed in Potassium Carbonate and Rongalite C. Solution.
5. Soda Ash, Dissolving Salts, Rongalite C. Process.
6. Vatted with weak Caustic Soda and Hydrosulphite. and printed in 40 to 45 deg. Tw. Caustic Soda, Rongalite C. Solution.

Colors which have proved satisfactory by these formulae, a few will suffice to illustrate:

1. Indanthrenes, Yellows, Orange, Red, Ciba Blue and Violet Paste Colors, etc.
2. Helindone Pinks AN, BN, Helindone Brown GN.
3. Indanthrene Blue RS, Indanthrene Brown B, Indanthrene Black B, etc.
4. Ciba Blue and Violet, Indigo 4B and MLB, Helindone Violet R, powder qualities, etc.
5. Hydron Blue G and R Powders, etc.
6. Indanthrene Olive G, etc.

New Silicate of Soda and Caustic Soda Substitute for Carbonate of Potash

During research work covering many years, the writer found that Silicate of Soda, in conjunction with Caustic Soda, formed an admirable substitute for Carbonate of Potash, and if used in the requisite proportions, gives results superior to those with Potassium Carbonate.

In support of the success of this Silicate Caustic Process the writer has applied certain Indigoid Dyestuffs (Ciba Blue, Ciba Violet, Paste and Powders) continuously in practice during a period covering several years, the resultant shades possessing an equally marked degree of brightness, more even and uniform prints, and also increased depth of shade.

The ratio of Silicate of Soda and Caustic Soda against Carbonate of Potash can be based on 66 parts of Commercial Silicate of Soda and 33 parts Caustic Soda, 90 deg. Tw., as against 100 parts Potassium

Carbonate of 90 to 92 per cent K_2CO_3 strength. The presence of an excess of Alkaline Hydroxide prevents any danger of precipitation, which, in the absence of Caustic Soda, would be liable to occur.

Silicate of Soda is found in Commerce in several forms, such as thick viscid liquids, thinnish syrupy liquids, and also in dry plate and powder forms. Some are highly alkaline, while others are nearly neutral. The composition varies from 24 to 38 per cent SiO_2 and from 6 to 24 per cent Na_2O, according to the different brands designated.

Usually a Silicate of Soda specially manufactured for Textile Purposes is obtainable, such as the "Star" brand, manufactured by the Philadelphia Quartz Company, which is admirably suitable for Calico Printing.

Various Assistants

It is perhaps worthy of note to here mention the influence that the addition of Glycerine has on the ultimate results. An addition of one part of Glycerine for every sixteen parts printing color is of a beneficial character in that Glycerine, being of a hydroscopic nature, retains a certain amount of moisture in the drying of the prints before aging, and also attracts locally the moisture during aging, thereby assisting in the reduction of the Vat Color. It must, however, be borne in mind that such an addition is, to a great extent, dependent on local conditions.

Various manufacturers of Vat Dyestuffs attach considerable importance to the use of Dissolving Salts (Benzyl Sulphanilate of Soda) in connection with the preparation of Vat Colors for Printing, and in a number of instances it is indispensable, i. e., such colors as Hydron Blues, Cibanone Brown R, and Helindone Brown 2R, Pastes or Powders.

It is essential that the Paste Dyestuff should be in a very finely divided state of suspension. The nearer it is to that of a Colloid State, the better are the results obtainable. It is not unusual to find a color from different manufacturers, even though it may be sold at the same strength of concentration, giving totally different results when applied under identical conditions. The physical appearance of the paste vat color is very often a good criterion as to results in this respect.

The writer had occasion to experiment with Indanthrene Blue GSZ Paste, which is a color specially prepared by the manufacturers for paper tinting or bluing of white goods, a procedure analogous to that of using Ultramarine in a finely divided state of suspension in water. This color gives excellent results when applied as a printing color, which bears out the above remarks.

It s only by a careful selection from the extensive available range of the present day Vat Colors that the best and most suitable is procured, for it does not follow that a color which is admirably suitable for piece dyeing will prove likewise so for printing and vice versa. Hence the desirability of close co-operation between Laboratory and Color Shop.

Notes on Aging

Important factors which add considerably to success in the application of Vat Colors, are ideal steaming and aging conditions. The Ager should be of the Hydrosulphite Type, containing water tank, contents of which should be maintained at a boil, the mouthpiece of the Ager should be of such a type as not to allow more than a minimum amount of air to enter with pieces. Also the ventilators should be regulated so as to allow for a copious exit of steam. The water tank should be well covered by baffled perforated sheets of iron in order to prevent the boiling water coming in contact with the cloth, but at the same time to allow the exit of the moist steam from the tank.

It is preferable to have a direct supply of steam from one Boiler in order to avoid, as much as possible, any fluctuation in pressure which is bound to be the case if the Ager is supplied by a main steam pipe.

The steam supply should register on pipe entering the Ager a pressure of 110 pounds per square inch, and by means of perforated iron pipe enter the water tank, and thence into the interior of the Ager. It cannot be emphasized too much that *moist* steam is an essential factor towards an ideal reduction of the vat colors as applied in printing.

The inside temperature of the Ager should register between the limits of 215 deg. to 225 deg. Fahr. dry bulb Thermometer, and 212 to 214 deg. Fahr. wet bulb Thermometer. Higher temperatures than 225 deg. Fahr. on the dry bulb Thermometer indicate dry steam which is not near so efficient.

Regarding the time required for the passage of the pieces through the Ager, a duration of five minutes usually effects perfect reducing, in some instances, two minutes suffices, as for example, in the Aging of Indigoes where a passage of longer duration brings about overreduction with ultimate loss in tinctorial value.

Drying

It is also important to bear in mind that overdrying of the pieces after printing should be avoided. If hot air drying is not applicable (for certain cloths this is essential), care should be exercised in seeing that only

the minimum number of drying cylinders are used in order to obviate overdrying or baking.

Washing Off After Treatment

There is everything in favor of taking the Prints straight from the Ager, and immediately subjecting same to the final treatment, thus avoiding possible danger of Lap marks and uneven oxidation. The prints are preferably washed with a copious supply of cold water, to which an addition of Bichromate of Soda is an advantage, in some instances followed by hot water in the open state, then soaped for a period of 10 or 15 minutes in the Rope form in order to remove all traces of unfixed color and also thickening. Soaping at the boil is indispensable in order to develop the true shade of color.

Remarks

It would be of very much help to the Printing Trade in general if an exchange of views could take place between competent authorities regarding such subjects as the one just summarized, for, no doubt, of recent years a large amount of unpublished research work has taken place, the value of which the Trade in general knows very little about.

Mr. Whittaker—I would like to bring to your notice a few swatches which have been done by this new silicate caustic process. If anyone is interested in seeing them, they may be passed around the room.

President Olney—I am sure there are many who would like to ask questions on this important subject. Mr. Whittaker said at the close of his paper that an exchange of views would be very valuable. Here is an opportunity for the next ten minutes to take advantage of that. He also states "an exchange of views among authorities would be valuable." As I look around the room I see several authorities on this subject.

Mr. Hirst—I would like to ask Mr. Whittaker if he has noticed any peculiarities, in the dye, of oxidation with Indanthrene Yellow; that is, compared with other vat colors.

Mr. Whittaker—Yes; it rather takes a longer time to develop it in the washing-off treatment and we generally find that the use of bichromate of soda is an advantage for that particular color.

Mr. Hirst—In that case, if printing greens, it is absolutely essential to select the proper blues?

Mr. Whittaker—For greens, we generally mix the Indanthrene Blue with the Indanthrene Yellow, but give an after-treatment with an oxidizing agent.

Mr. Hirst—I have noticed that if you subject such a green to simply washing in cold water and then boil in soap, even for fifteen minutes, when those goods are finished and put into the folding room or packing room, in perhaps two or three hours that the blue will develop. Wouldn't you think, naturally, that a reduced yellow would have dissolved off in soaping?

Mr. Whittaker—In treating yellow, give it plenty of cold and hot water before entering the soap; in fact, the success of the development depends on giving hot water previous to soaping. The blue itself will develop quite nicely with cold water—I am speaking in regard to printing. If you give Indanthrene Blue the treatment in bichromate you will probably find it brings your shade along, and you lose that beautiful reddish tone by giving the chrome.

Mr. Fernald—I would like to ask Mr. Whittaker if there isn't some objection to that caustic soda silicate method in regard to the method of handling, from the disagreeable action that comes from such a combination in the color shop and also from the printers and the rollers. By the glucose soda-ash method in combination with sulphoxalate, you not only eliminate the amount of sodium sulphoxalate that is necessary for reduction, but also you eliminate the disagreeable handling of a very strong alkaline solution in the process.

Mr. Whittaker—Well, you cannot say that it is very strongly alkaline. I will just put it to you as I see it: When I introduced this process, our colorist said, "Keep it away from us; it is too strongly alkaline."

I said, "Well, you go to work and try it"; and we are using it now at the rate of about two tons per month of silicate of soda, which equals about three tons of carbonate of potash. We have had no trouble regarding the working of the colors. In fact, our colorist would rather to-day strain 40 gallons of silicate color than he would 40 gallons of carbonate, because it goes through the strainer more easily. In fact, my people swear by it.

Arthur R. Thompson—I should like to ask the experience with regard to printing vat colors in an acid paste.

Mr. Whittaker—I have had no experience whatsoever other than in an alkaline solution. That is something new to me.

Mr. Thompson—You speak about the use of dissolving salts in connection with the preparation of vat colors for printing being indispensable with Hydron Blues and Helindone Brown. I wondered if you ever tried to use more of a reducing compound instead of using that dissolving salt?

Mr. Whittaker—On practically every color I have tried I have gone from a minimum to a maximum amount of Rongalite, and with those particular colors, for regular working, we have to have the dissolving salt.

Mr. Thompson—Have you ever had any experience in the discharging of these colors?

Mr. Whittaker—Practically none to speak of, other than in very faint tints, not dyes.

President Olney—I might say if there are others here who can answer questions like the last one, in regard to discharging vat dyes, we should be pleased to have them do so, and I am sure Mr. Whittaker will be glad to have them supplement his remarks.

George A. Moran—Do you use this formula generally for all your colors in printing, or do you use a number of different formulas?

Mr. Whittaker—As I mentioned, we have about six formulas in use for the different colors; some colors prefer strongly alkali, and others prefer weakly alkali.

Mr. Moran—Isn't it a disadvantage to have so many formulas in use at one time?

Mr. Whittaker—If we produce regular work by the use of six formulas, it is better than having one formula and producing uneven work.

Mr. Moran—Couldn't you pick a line of colors that would all work with one?

Mr. Whittaker—Not if you wanted the highest degree of fastness. You could pick out a range of colors and use one formula, but you wouldn't have the best and the fastest colors in that range.

Ben Verity—I might say that in Canada they seem to have a better grade of help than they do in some mills in this country. (Laughter.)

Mr. Hirst—Do you find that there is any particular advantage in the initial reduction of the vat colors by using the hydrosulphite powder and then mixing in the formaldehyde compound as a subsequent agent?

Mr. Whittaker—With the powder, it is almost necessary. With the paste forms we don't use the hydrosulphite powders whatsoever. It is only in the case of the powder form that we do.

President Olney—Are there any further questions?

Mr. Moran—Would you, in using these different formulas, mix colors that were made up by two different formulas?

Mr. Whittaker—You might repeat that question.

Mr. Moran—Would you, in using your colors, mix colors to get a mixed shade which were made up by different formulas?

Mr. Whittaker—In making mixtures like that, we make a study of the colors and the recipe by which we apply them, and if we want a mixture we generally try to obtain that mixture from colors that are put together with the same recipe. We wouldn't take a yellow which was applied in carbonate and mix it with a blue that was applied in a strongly alkaline solution.

Mr. Thompson—If you have Naphthalene Green, would it be possible to mix that in with some vat colors?

Mr. Whittaker—What would be the object of putting a sulphur color along with a vat color?

Mr. Thompson—It is cheaper.

Mr. Whittaker—But you lose your fastness on the vat color by putting the sulphur color in it, which will not stand chlorine.

Mr. Pratt—I would like to ask Mr. Whittaker what dissolving agent he mentioned.

Mr. Whittaker—Well, the alkali and the hydrosulphite, and if you use acetic acid, glucose with the acid.

President Olney—I think Mr. Pratt refers to that dissolving salt you mentioned.

Mr. Pratt—I understood you recommended a dissolving salt and I wondered what it was.

Mr. Whittaker—It is benzyl sulphanilate of soda. I don't know whether it is manufactured in the States or not.

President Olney—I would like to say in connection with the discussion on this paper that in reply to the questionnaire we sent to the members, there was probably a call for a discussion upon vat dyes from a greater number of individuals than for a discussion of any other subject, and this afternoon, if there is time, we will have a general discussion upon vat dyeing. Furthermore, I might say that as the afternoon session is very full, if there is time this morning at the end of the session we may spend a few minutes in a discussion of vat dyeing.

The next paper, "Color Matching as a Factor in Accurately Rating the Relative Values of Dyestuffs," will be presented by H. S. Busby. (Applause.)

. . . Mr. Busby presented his paper extemporaneously in abstract, but subsequently forwarded to the Council the following version:

COLOR MATCHING AS A FACTOR IN ACCURATELY RATING THE RELATIVE VALUES OF DYESTUFFS

By Hibbard S. Busby, *Research Colorist*

It is essential that the terms of this subject be clearly defined, in order that the subject matter based thereon be as definite as possible and that the statements made may be aligned with common experience.

By Color Matching we refer to the whole group of methods of optical-physical measurement including colorimetry, photometry, spectroscopy, etc., which are necessary to the colorist if he is to accomplish accurate estimation of the small differences encountered in colored solutions and dyed materials, as well as the nature of these differences. It is realized that this is a very great enlargement of the usual term, but has been used, in this case, to connect the older art with the present technique.

In speaking of Values we refer to those useful properties of a color, by the observation of which we determine its adaptability to our uses. These properties include strength or concentration of color, tinctorial power, purity (freedom from degradation or other mixture effect), etc.

The industrial requirement of color demands accurate

The above photograph shows a group of those attending the morning session. It was taken on the roof of the H mechanism of the camera, and were not apparent until the film was developed. Original copies, thirty-six inch

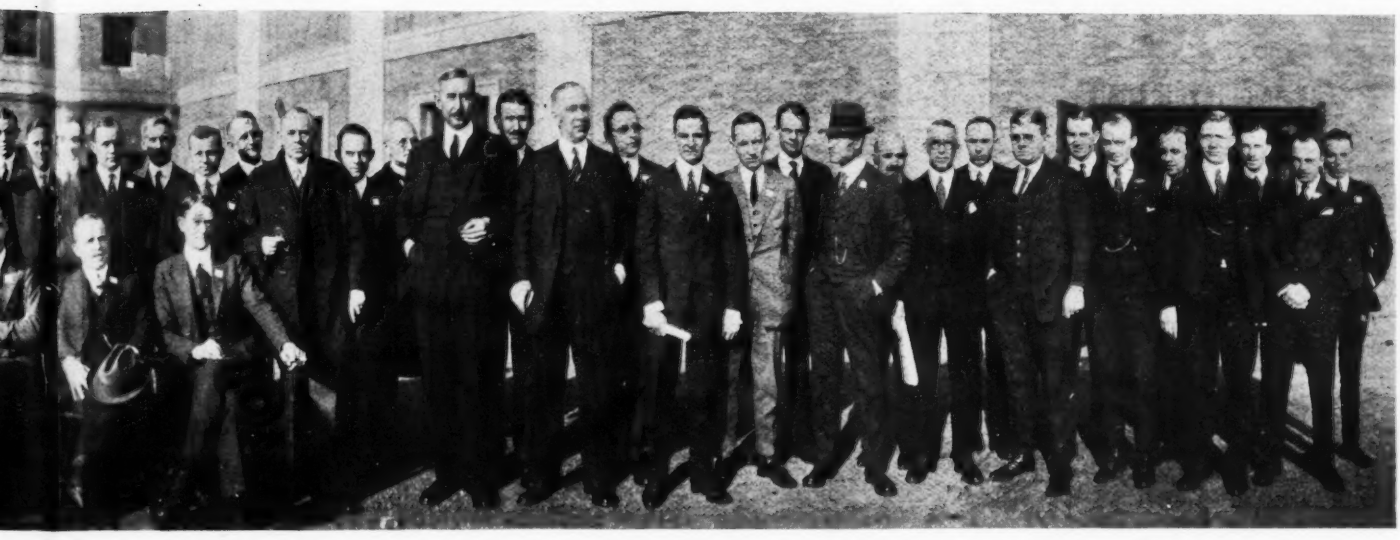
determination of several properties, which may be stated, briefly, as follows:

1. For several given dyestuffs it is desired to know their relative dyeing power per pound of dyestuff used, based also upon the relative cost of each. The ultimate determination of this is the quality of the dyed color or the dye solution when this dyeing, or solution, has been made up (in each dyestuff being prorated) in the percentage ratio of cost it bears to all the others.

2. It is essential to be able to determine such variations from standard as slight hue differences for a given percentage of dye concentration, the intensity of the dyeing for a given percentage of dye, and whether the resultant color produced by successive stages of dyeing in small concentrations is the equivalent in result of that produced, by other material in one process. Exact matching is a very important aid, also, to the estimation of results in slight changes and detailed steps of the study of control of process from the laboratory.

For ordinary routine work where the requirement is not for any absolute degree of quality the trained eye has been used as the final arbiter since the beginning of the art. In a sense the success of this method has been that such use of the eye had the advantage of intimate association in its every-day task with such perfectly harmonious product that very slight errors and degrees of off-shade were readily noticeable. That method of matching was the product of a period when every process man was on a highly competitive status as regards the *artistry* of his product, hence the degree of refinement to which the method was developed. Our present age has, unfortunately, no parallel to this condition and the means of science must be employed to make accurate, reliable determinations of the results of production. It is perhaps fortunate that any means at all should be the means of bringing about our turning to technical methods of analysis, because when the present murmur of artistic tendencies in modern life has risen to a scale comparable to that of previous ages it is to be hoped that the technique developed in this intermediate period will provide us a means of permanently recording the facts and the method of our art, and that never shall the future world be able to speak of any of the finer works of our present day as "lost art."

When the eye is assisted by mechanical-photometric aids, and the proper surroundings created for observing material (dyed fabric, dyes, mixtures, etc.), the ability to judge very slight differences in quality is thereby increased, and the results of close, quantitative process work with dyes, etc., can be, therefore, very much more accurately determined. This is particularly true where the small quantity stage of the work (in the laboratory) must be translated in terms of the large stage (process) and for such quantitative work as the standardization of dyestuff stands, formulas, etc., it is the only means by which such multiplication or amplification of results can be carried out with confidence. In any case where *relative measures* are necessary on dyes which are not subject to complete chemical alteration during their process of application, the colorimetric method, in the hands of an experienced technician, offers more accurate and reliable means of investigation than any methods previously reported; wherever this method is properly carried out not only is more reliable data obtained, but a great many types of information about properties and nature of materials and processes are obtained which previously



of the Hotel Pennsylvania after adjournment for luncheon. The vertical streaks were caused by slips in the revolving -six inches in width, may be obtained from Charles F. Allen, 216 West 104th Street, New York City, for $1 each

were unknown, and no other method is known for securing them.

It is unfortunate for a printed article that so much of this sort of data requires the comparison between graphical analysis results and the actual appearance of the material under study. However, a plate is included (see page 20) which shows the difference between two dyed lots which by comparison before the unaided eye yielded no quantitative data of value in the process, whereas the plotted data aligned accurately with the quantitative change which brought the process back to standard.

All this work is but part of a noticeable tendency which is on the increase recently—the study of physical phenomena rather than reliance entirely upon chemical analyses. The explanation of a great many phenomena, even chemical phenomena, may be found in physical analysis, indeed much of the progress in the work of the British Society may be traced to the fact that many of the dye researches of that Society have been along the lines mentioned above. It would seem that a proper correlation of these efforts would be a very forward-looking step in the art of dyestuff application and would furnish, ultimately, complete knowledge of the properties of the materials in the handling of which we are engaged.

President Olney—This whole subject of small differences in color matching I know has been a puzzle to many of us at times and any method or any device which will make it possible to measure these small differences will be very valuable indeed. Up to the present time, as far as I know, there is no apparatus which is at all perfect in this respect; in fact, they are very far from it. Those which are of value as far as matching colored light is concerned are of little value as far as colored textile material is concerned, and there is a constant call for some type of apparatus that will measure the color on a dyed fabric in such a way that that record may be kept as a standard and referred to six months or a year later. There are several devices which it was hoped would accomplish this, but as far as I know, none are satisfactory. I think there is an opportunity for more or less discussion on that subject. There are several present that I know have thought a great deal about it. We shall be glad to hear from Dr. Rose.

Dr. Robert E. Rose—I should like to ask Mr. Busby whether I am right in assuming that what he has said of the measurement of the physical constants by physical methods can be used as a means of standardizing color value, for instance, in purchases of color?

Mr. Busby—Answering that question of Dr. Rose, I can say: that in the case of three dyestuffs that are pretty closely grouped together in properties, suppose that percentage dyeings have been made of each on the ratio of the relative cost (per pound), so that the appearance result on those patches would show how relatively "color-valuable" they are to us if they all cost the same. Having done that, the resultant color measurement of your colored patches will show you these factors: viz., (1) the factor of purity of hue, (2) the concentration or strength of the color, and (3) you can make, from a spectrographic study of those same patches, a determination of the maximum and minimum dyeing power of each. You can get only a certain amount of a given color on a certain cloth and it has been shown in practice that the spectrographic study of the dyestuff when dyed on cloth

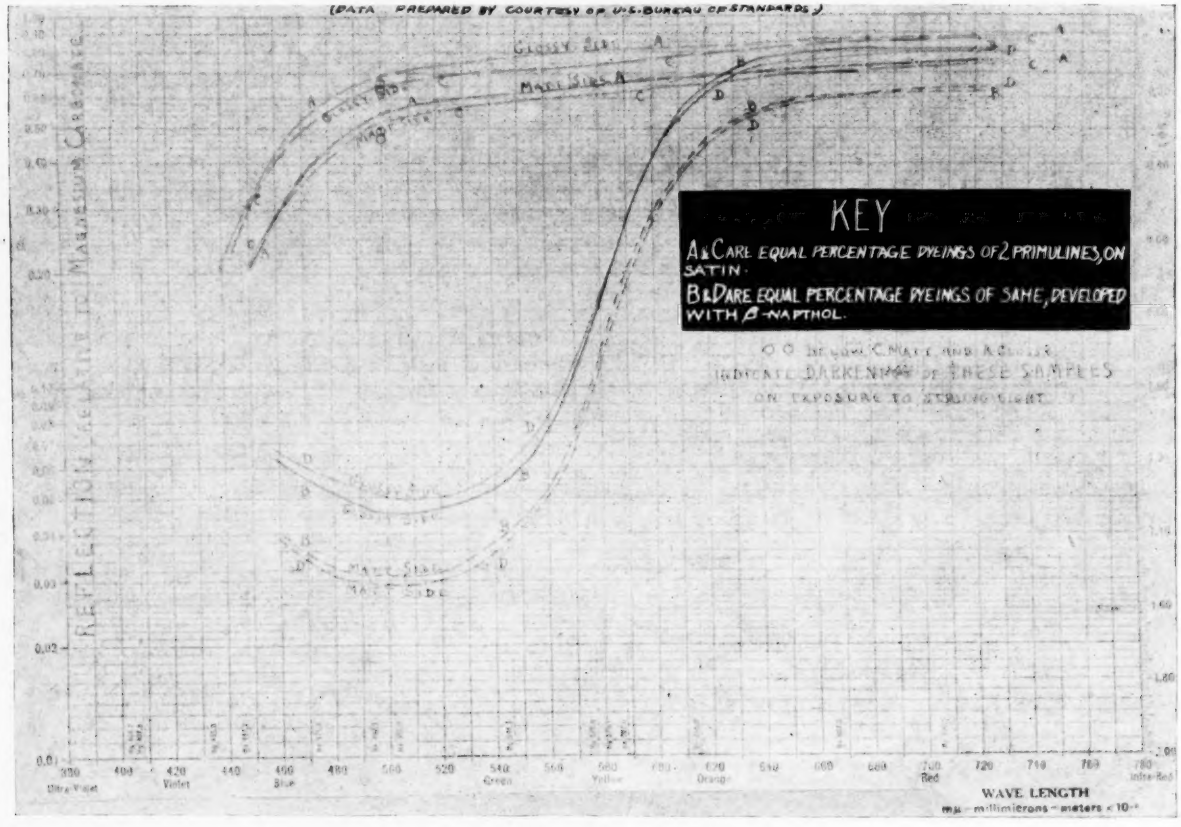
in a number of different percentage ranges shows conclusively you have the strength limits to which you can dye a given hue in that particular dyestuff. That is very definite information.

It is pretty hard to explain this matter in words alone, without diagrams and solutions, but it means this: that the information (obtained by physical measurement) which you get from the color, together with certain general information (as proportion which bleeds off, etc.) gives you means to calculate the limits beyond which you cannot hope to go in concentration of a given dyestuff in order to produce a given hue. In other words, it shows us this about dye formulae: that there is no hope in taking certain colors for certain dye formulae, because even though you increase the concentration you cannot increase the dyeing power.

I would like to say one thing, in regard to what Professor Olney said on the subject of instruments. There has been great hope in the textile trade of developing some sort of "instrument-for-all-outdoors." In fact, it seems as though one of the demands of the textile trade is that whenever an instrument is talked of, or a method is talked of, it should be all-inclusive—sort of an Aladdin's lamp. I am not going to say that the thing can't be done, but I will say it isn't the thing we ought to do at the present time—that the problem is so clear-cut in a great many divisions of the work that it is cheaper and better; in fact, it is an economic proposition, to make use of small devices for doing certain particular classes of work, rather than one expensive device that will attempt to do all of these different things.

Recently, I saw some instrument data made by a paint manufacturer on the general subject of bringing up the purity of one of his pigments. He had the data right in hand but he was utterly unable to interpret it. He had all the necessary information there to enable him to change the process, and if he had had the proper physical knowledge to enable him to interpret the information he could have gone ahead and made the change. As it was, he said to me, "The instrument isn't worth a damn." [Laughter.]

I submit to you that that is a factor for which there is no substitute—*knowledge*, and knowledge of the situation.


(DATA PREPARED BY COURTESY OF U.S. BUREAU OF STANDARDS.)
KEY
A & C ARE EQUAL PERCENTAGE DYEINGS OF 2 PRIMULINES, ON SATIN.
B & D ARE EQUAL PERCENTAGE DYEINGS OF SAME, DEVELOPED WITH β-NAPTHOL.
WAVE LENGTH
mμ - millimicrons - meters × 10⁻⁹

Reproduction of Chart Referred to by Mr. Busby on page 19

Dr. Rose—The point that I see, then, is rather that it allows you to discriminate between different colors of the same hue, if you have them, with the same general properties, if you want to make a mixture. Is that really the essential thing?

Mr. Busby—That is one of the things.

Dr. Rose—And it would not be suitable just to determine the strength of a dyestuff because it is very difficult to define strength in terms of physical data?

Mr. Busby—We have some information on the subject of inherent properties of dyestuffs and among other things we know this: that if we make a physical study over certain concentration ranges of a given dye, that is, the dyestuff solution and dyed patches are prepared in various concentrations and conditions and studies made of these, we derive information through which we can prorate any group of the dyes in the same class or of a similar nature, or the absolute properties of any single dye. That is true of any dyestuff, and I wouldn't give you the impression that it is *only* a question of comparative values as between several dyestuffs of a group. It is more. Supposing, for instance, you want to get a yellow or a green or a blue, and you haven't any particular choice of the dyestuff you can use beyond the choice of the material which you are going to dye; if that is the case, you can select from any one of the dyestuffs available for dyeing that fiber the dye which has the strongest dyeing powers, by means of physical measurement.

President Olney—Is there any further discussion of this paper? If not, we will pass on to the next one entitled "Starch: Its Use in the Textile Industry," by Dr. W. R. Cathcart.

Dr. W. R. Cathcart—Mr. Chairman and Gentlemen. I would like to say at the outset that I accepted the invitation to read this paper with a great deal of hesitancy and I told your Committee very frankly why I was rather reluctant to do it. I somehow feel that considerable criticism has arisen of people who are connected with organizations that have something to sell who address organizations which represent the consumer. But it seems that these gentlemen felt perhaps what I had to say might be of some service, and therefore I was very glad to accept on that basis.

. . . Dr. Cathcart then presented his prepared paper, as follows:

TEXTILE APPLICATION OF CORN STARCH AND DERIVATIVES

By Dr. W. R. Cathcart

Corn Products Refining Company, New York City

A brief outline of the manufacturing processes is an appropriate introduction to a discussion of the uses and application of corn starch and the numerous products obtained therefrom, which for the want of a more comprehensive term are designated as derivatives.

As is perfectly well known to all present, the crude starting material is the grain of corn. This grain of corn has on its exterior an integument which is generally termed the hull, then comes the endosperm or main portion of the grain, which is a mixture of starch and gluten, the nitrogenous portion of the grain, and last is the germ or fatty portion. The first aim of the process is to get these various constituents of the grain to part company so that they may be collected separately and each then put to its own proper use.

Steeping

The grain of corn when taken from the fully matured and dried ear is a hard, flinty, fairly brittle mass. This character is changed by steeping with moderately warm water for several hours. The grain swells and softens to such an extent that it may be crushed, not so easily but somewhat after the fashion of a grape; that is the hull slips off, the germs frees itself from the endosperm and the endosperm is fairly well disintegrated. The steep-water dissolves a certain amount of soluble matter which is valuable. Subsequent evaporation and concentration of the steep-water put these water soluble constituents in condition for utilization.

Grinding the Steeped Grain

The steeped grain after having been freed from the steep-water is subjected to a coarse grinding or disintegrating process, which tears apart the various portions of the grain so that they may be conveniently separated by mechanical means. The fairly wide range of specific gravity shown by the different constituents permits the use of water flotation for such separation. The germs being lightest of all are skimmed off the surface of the water, dried and passed on to other processes.

Fine Grinding and Reeling

The water suspension of hulls, starch and gluten is subjected to a series of fine grinding and screening processes and thus is accomplished the separation of the hulls from the mixture of starch and gluten. The hulls are collected on the sieving reels, dried and passed on to their proper utilization.

Tabling

After the complete separation of the hulls, the finely ground starch and gluten are in the form of a water suspension of a fixed specific gravity having cream yellow color. This starch-gluten suspension is allowed to flow slowly into long, narrow, comparatively shallow, troughs or "tables" which are slightly inclined. The stream of starch and gluten falls on the table in a small stream at one end and gradually overflows at the

other. During the course of this mixture through the trough, a fairly good separation of the starch and gluten is accomplished. The starch having a higher specific gravity than the gluten precipitates and forms a cake on the table while the lighter gluten and a small amount of starch overflow with the water at the far end of the table. This gluten and the accompanying starch are collected, dried and used for purposes outside the scope of this discussion.

Pearl Starch

The starch which settles out on the tables still contains a small percentage of gluten in the same way that the gluten which overflows from the tables contains a small percentage of starch. The starch on the tables may be handled in two ways. It may be removed from the tables and again suspended in water and again run over the tables; in other words, retabled, in which case further elimination of gluten and other impurities is effected and finally when dried yields starch of great purity. On the other hand, it may be transferred from the tables and subjected at once to the drying process without retabling. Such a product is the ordinary Pearl Starch of commerce. This is the crudest form of corn starch which is commercially possible, and since it serves as the crude material for the purified, modified forms of starch and all other products made from starch, has been very aptly termed the "pig-iron" of the starch industry.

In order to avoid confusion and misunderstanding, it might as well be explained here that the designation "Pearl" has gradually come to have a double meaning, that is, it sometimes designates physical form as well as quality. When wet starch in the form of large lumps or cubes is dried very slowly, the dried cubes fall apart into irregularly prismatic, elongated forms which are commonly termed crystals. If these crystals are carefully handled and packed, they finally reach the consumer as "Crystal Starch." If, however, the wet starch is shoveled onto trays or into racks and dried in a shorter time, a mixture of powder with granular particles and some small crystals results. This condition is what is known as "Pearl Forms." A purified and modified corn starch may therefore be delivered in pearl form as well as crystal form, whereas the crude, unpurified starch is alway delivered in "pearl form," and unless otherwise specially indicated "pearl starch" represents the first separation of starch without further purification.

Pearl starch is the crude material for all products made from starch such as purified starches, modified starches, dextrines, gums, corn syrup and corn sugar. In spite of the fact that "pearl starch" does not represent a high degree of purity, its use in the textile industry is fairly extensive. There are many cases where lack of exacting specifications permits its use, such as: warp-sizing in the coarser grades of work and in cases where the retention of the starch by the fiber is not of first importance, finishing and back filling to a lesser extent.

Purified Starches

Starches are purified either by powdering and bolting or by retabling (washing) or by a combination of both. If ordinary "pearl starch" after drying is powdered and bolted through bolting silk quite a marked purification takes place. Of course, no soluble impurities are removed by this process, but the percentage of gluten is reduced and all hard particles are removed, and the product after such treatment has a much higher sizing and finishing value than "pearl starch." When "pearl starch" is retabled soluble impurities are removed and reduced to a minimum. Retabled starch, when dried slowly, yields the crystal starches, when dried more rapidly, the purified "pearl form." This latter form may be powdered and bolted and gives a purified powder. Such forms are used for warp sizing, finishing, etc., where the conditions are more exacting.

Modified Starches

The tabling, powdering and bolting processes just mentioned of course do not alter the character of the starch as such. The starch remains the usual thick boiling type, that is, forms a thick paste when boiled with water in the proper proportion. The character of the paste formed may be altered by modifying or changing the starch to a thin boiling type or to an alkaline thick boiling type.

Thin Boiling Starches.—Purified starch when hydrolized changes into dextrine, and dextrose. With proper conditions of concentration and temperature, hydrolytic action may be induced and then checked in incipient stages so that no appreciable quantity of dextrine or dextrose (both water soluble) is formed and the starch still remains starch. By varying the conditions of concentration, temperature and time of action, a series of starches are obtained which differ very markedly from the original starch from which they are derived. When pastes of these starches are compared with a paste of the unmodified starch of like concentration, they are found to be very much thinner and give the impression of being of lower concentration than the paste made from the unmodified starch. For this reason, such starches are very properly called "thin boiling starches." Quite commonly these thin boiling starches are erroneously called "soluble

starches." They are made by a wet process and separated from the water solution by sedimentation, so that all solubles except the small amount contained in the adhering water would be removed and lost. There is no such thing as a commercial soluble starch.

Starches forming pastes of different degrees of thinness are obtained by checking the process of incipient hydrolysis at different stages. These processes have been standardized to produce commercial starches of five or six degrees of paste fluidity, which range is sufficient to meet the various needs of manufacturing operations. It is evident that thin boiling starches may have pearl, powdered or crystal form.

The successful manufacture of thin boiling starches on a commercial scale stands out as one of the most important accomplishments in the recent years of the industry. The regulation of the processes and the standardization of the products require much care and close control. The introduction of these starches to the textile industry necessitated a slow but effective process of education. Their value and importance in warp-sizing, finishing, printing and dyeing is now very generally recognized.

Thick Boiling Alkaline Starches.—Normally, all starches have a very slight acid reaction. Absolutely neutral starch is not a commercial product. The so-called neutral starches are left just sufficiently acid to be sure they are not alkaline. This acidity is usually about 0.06 per cent. Alkaline Starches are made purposely so by an alkaline treatment and for the most part show an alkalinity of approximately 0.125 per cent. These starches when boiled with water form thicker pastes than unmodified starch and of course much thicker than the thin boiling starches. This property makes them adaptable for certain finishing processes. They are also used in connection with dyes where an alkaline reaction is not objectionable. While still used for warp sizing, they have been superseded in most cases by the "thin boiling starches."

Dextrines and Gums

Dextrines and British Gums are obtained from starch by a process of roasting or heating at a moderately high temperature, with or without the addition of small quantities of acids. This treatment converts the starch partially or completely according to the conditions of time, temperature, etc. A low conversion gives a white or light colored dextrine of low solubility; a high conversion gives products progressively darker in color and higher in solubility. Apart from differences in color and solubility, these products differ very importantly in other physical properties, particularly paste forming qualities. Such differences cannot always be determined by chemical analysis. The recent development of the plastometer has thrown some light on this subject, but there is still much to be learned in this direction.

Corn Dextrines and Gums have a wide application in the textile industry more particularly in finishing, printing and dyeing operations. The effects desired and the conditions of work must determine the type to be selected from the very wide range which is offered the industry.

Corn Syrup and Corn Sugar

Corn Starch is converted into Corn Syrup or Corn Sugar or Dextrose by the action of dilute acids combined with high temperature and pressure. While it is possible to obtain practically chemically pure dextrose by such conversion or hydrolysis and subsequent purification, technical corn syrup and corn sugar contain certain percentages of dextrine which will vary according to the conditions of the conversion. The textile application of corn syrup, commonly referred to as glucose and corn sugar, is not so extensive as that of starch and dextrine, but they have been found useful for certain special effects.

From the foregoing limited discussion, it is clear that a large variety of products are obtained from corn for use in the textile industry. Starches and Dextrines from other sources, such as potato, wheat, rice, sago, tapioca, etc., are available, but in no instance has the starch industry been so broadly developed or so highly specialized as is the case with corn starch. Continuous operation on a large scale as against intermittent, limited activity has made this development and specialization possible. Uniform standard products are indispensable to uniform results. The textile demands grow more and more exacting as the industry grows and extends. This has resulted in a mutual stimulation. The starch manufacturer is moved to meet new demands and, on the other hand, offers ideas and products in the line of improvement in regard to quality and cost.

Those who might have expected from this discussion any dogmatic statements that such and such starches, dextrines, etc., must be used in just such and such a way to produce certain desired results, will be disappointed. Such questions are frequently far more complicated than most of us realize. Proper recommendations can be made only after examination of the conditions prevailing in each individual case and must be based upon a frank discussion of the conditions and the results sought. Many know that there are several kinds of starches and dextrines, such as corn, wheat, rice, potato, sago, tapioca, etc., but many do not know, for instance, that there is a large variety of corn

starches and dextrines which differ from each other in many instances just as much as they do from similar products derived from other sources. Suppose, for instance, a starch or dextrine consumer is dissatisfied with the lack of uniformity or purity or the character of the product in use, it may be corn, potato, sago or any other. If he does not know that there are such products as thin boiling starches and thick boiling and in fact different varieties of these types, the difficulty may remain unsolved for a long time. The fact that difficulty has accompanied the use of potato starch and "pearl starch" should at once open the way for an investigation of the purified and modified starches. It is difficult to combat the traditions and rule of thumb methods of any industry. The progress of an industry is intimately affected by the progress of the industries which serve it. They must move together in the same direction. Such co-operation is mutually beneficial and must be based upon scientific method, confidence and frankness.

President Olney—I think every textile chemist realizes the problems with which he is confronted when he begins to work with starch. A chemical analysis in many instances means nothing at all. Two starches, as far as chemical tests are concerned, or two finishing products might give exactly the same chemical analysis and yet act entirely different in actual use. So anything that is of light along this line is very valuable indeed.

Take the case of the woolen industry: the cotton industry, of course, uses enormous quantities of starch; the woolen industry uses comparatively little. The cotton industry recognizes the fact that the warp must be sized. In the woolen industry there seem to be two quite different points of view; in some cases they will size the warps with glue; in other instances they will not size them at all. Between these extremes, of course, we have opportunities for using starch.

I would like to ask Dr. Cathcart to what extent starch is used in the sizing of warps in the woolen and worsted industry?

Dr. Cathcart—The use of starch for sizing woolen warps is much more extensive in England than it is in this country. As far as I know, its use is very limited in this country. I know they are using it to a great extent in England. I was over there to the World's Cotton Conference in 1921 and investigated a good many plants over there.

President Olney—I have one other question: I would like to know if you can tell us anything about the product that is made by treating starch with calcium chloride. Have you run across that at any time? Do you know what its chemical character is?

Dr. Cathcart—I doubt very much if anybody knows whether or not any true chemical action takes place between the starch and calcium chloride when they are mixed together. It does have a very marked physical effect in the kind of jelly that is produced and such mixtures are used quite extensively by the so-called sizing compound manufacturers. In my opinion, it has the value of giving you a calcium chloride in a rather convenient form to handle—that is, if you want calcium chloride in your sizing mixture—on account of its hydroscopic properties. Of course, that is the only value calcium chloride has in the sizing mixture. The finishing people very properly object to the presence of calcium chloride.

President Olney—It is, then, a mixture rather than an actual combination?

Dr. Cathcart—It produces the well-known form of jelly; it looks just like gelatin and it gives you calcium chloride in a convenient form to handle. You don't have to break it up and mess up the place by weighing out a certain quantity; you have this thing already prepared, which keeps nicely in a barrel, and you can measure it out and put it in your mixture to suit yourself.

Winthrop C. Durfee—I would like to ask the Doctor if he can give us a statement as to the chemical differences between sugars of glucose (the commercial forms) and grape sugar. There seems to be a choice in the use of those two in, for instance, the reduction of chromium salts for the forming of tannin liquors, and there seems to be a practical difference in the effect, or handling. There is some difference, I know. A table of the distinction between glucoses and crystallized grape sugar as to the sugar contents, was published some years ago.

Dr. Cathcart—Crystallized grape sugar is, I am quite certain, a dextrose—

Dr. Durfee—Not wholly.

Dr. Cathcart—There may be a mixture of some levulose there, but the reducing power will be the same. We have, not only on a very large scale, but what you might call a semi-commercial scale produced a chemically pure dextrose from our corn sugar. Whether the reducing property of that, in reference to dyestuffs, as compared with ordinary grape sugar, is different or not, I really am not prepared to say.

Mr. Durfee—The difference between glucose and what is properly known as—

Dr. Cathcart (Interposing)—When you speak of glucose in trade you mean a liquid, a syrup, which varies in specific gravity according to the amount of concentration to which it has been subjected. You get a 42, 43 or 45. Now, if the conversion has been carried on so that you get a higher degree of purity, that is sugar purity, and a smaller percentage of dextrose, then that is a condition which produces crystallized sugar; that is, you can get it in lumps or slabs or chips. If that sugar is further

purified it eliminates the dextrin, because both glucose syrup, or the commercial glucose, and the commercial corn sugar contain certain percentages of dextrin that can only be removed by a rather expensive method of crystallization. And when you remove that then you get a dextrose that will run 99½ to 99.98 per cent pure.

Mr. Durfee—That doesn't answer my question. My question was as to the proportion in glucose and the proportion in ordinary grape sugar.

Dr. Cathcart—I haven't those figures in my mind right now, because we make several grades, but I will be glad to write you that information. The percentage of dextrin is higher in the glucose than in the solid sugars, and when they are purified it is reduced to a trace.

Mr. Livermore—I heard the speaker state that he did not think starch was used in this country to any great extent as a sizing material in the woolen industry. I would like to inquire if he meant to include in that statement starch as such only, or the gums derived therefrom?

Dr. Cathcart—I was only speaking from my own contact in that respect and my impression is that starch is not used as widely in sizing of woolen warps in this country as it is abroad. They may also use some dextrins, but if they do, they are not using what I would consider the best product for their work. I think they would get better results from sizing with the starch mixture than sizing with the dextrin mixture.

Mr. Livermore—Your opinion was expressed then only as to starch itself?

Dr. Cathcart—Yes; I think they are using some dextrin in that.

Mr. Beattie—I would like to answer Prof. Olney's question as to the use of starch in the woolen industry: Starches are not used extensively in the textile industry in Great Britain for woolens, except in the Spring Valley trade, in the low class goods. The amount of solubilized starch used in England is relatively large, for weighting of the filling only. The amount of starch consumed in the woolen end of the textile industry in Canada amounts to almost nil.

President Olney—Are there any other questions?

Mr. Chamberlain—A question was raised a moment ago by Mr. Durfee that I thought was not completely answered by Dr. Cathcart, in regard to the amount of dextrin in glucose of the different degrees, and in sugar. Am I correct in the way I stated that question?

Mr. Durfee—Yes.

Mr. Chamberlain—I believe I can throw a little light on that.

Commercial glucose has 45 per cent reducing sugar of the dry substance present. The dry substance varies from 21 to 13 water; the rest is dry substance. Forty-five per cent of that is almost exactly reducing sugar and the remainder is a mixture of dextrins that have not altogether been separated and separately named. Seventy sugar and 80 sugar—the two corn sugars—are converted to about 90 per cent purity, or 10 per cent dextrin, and they vary in the concentration. The 70, or tanner's sugar, is concentrated to 41 deg. Be., and is crystallized in a non-crystalline form; we call it crystalline; it is amorphous. The 80 sugar is boiled to 45 deg., but the purity is the same in each case until you proceed, as Dr. Cathcart has said, to remove that little dextrin that is left, which is essential for some limited purposes.

Mr. Durfee—It is 90 per cent dextrin?

Mr. Chamberlain—Ninety per cent reducing sugars. Sometimes you get maltose there. We don't know what is there; we get some very curious things sometimes.

Mr. Fernald—I would like to ask Dr. Cathcart if there is any objection to leaving the gluten present for the application of starch as a warp sizing or back filling, where a certain amount of adhesion is necessary for holding the starch in the goods?

Dr. Cathcart—Well, to the extent that gluten is present, you lose starch value, because the corn gluten is not like wheat gluten; it has no adhesive value at all. It is insoluble. It is only because that small amount which is there does not interfere, that permits the use of starch with gluten in it. You don't get any value from it.

Mr. Beattie—I would just like to say with regard to the presence of gluten in starches for sizing that the presence of a certain amount of gluten for sizing in the carpet industry is an advantage rather than a disadvantage.

Dr. Cathcart—That is wheat gluten, not corn?

Mr. Beattie—Yes, wheat gluten.

Mr. Christison—I would like to ask Dr. Cathcart what particular difference he notices in the pearl starch or the unpurified starch, as compared with the purified, with regard to its adhesive qualities on the warp yarn; that is, do you find that the purified starch will dust off less in a loom than the unpurified?

Dr. Cathcart—Well, I don't know that you would find such a marked difference between the purified and unpurified starches, as such, in that case. You would find, however, a very marked difference between the unpurified starch and the modified thin boiling starch, because the thin boiling starch has greater penetrating quality and you get an internal cementation rather than an external coating. To that extent, you do obviate practically all the shedding.

Mr. Christison—Have you been able to prove that a cotton or woolen fiber when sized with a thin boiling starch actually contains the starch material on its interior?

Dr. Cathcart—The best answer I can give to that is: I published a little over a year ago a review of a report that was made by F. J. Hoxie, which report was the re-

sult of an investigation he made for the interests with which he was connected. He made cross-sections of single strands of yarn, made photomicrographs of those, and they showed very definitely that the distribution and penetration of thin boiling starch was very superior to that of the thick boiling starch.

Mr. Christison—It is my opinion that even though the starch is soluble and might penetrate the fiber, it wouldn't have any effect on the sizing properties. I don't see how the penetration can really help the sizing at all. I should think that the sizing would be more of a surface effect; the sizing would cover the fiber more or less and perhaps attach one fiber to another, and that any material that would actually penetrate the fiber wouldn't be of much advantage.

Dr. Cathcart—Well, the sizing mixture does not actually penetrate the fiber. If I used that expression, I want to correct it. It penetrates the yarn. In other words, it penetrates between the individual fibers there and cements them together, and the breaking strength of the yarn sized with thin boiling starch as compared with ordinary or thick boiling starch is very markedly in favor of the thin boiling starch.

Mr. Christison—That is one thing we ought to be careful about in speaking on this subject; we are perhaps prone to say that the size will penetrate the fiber, rather than to say that the size will penetrate the yarn.

Dr. Cathcart—That is quite correct.

President Olney—Are there any further questions?

A. C. Persons—I would like to ask if there is a standard method of determining the paste strength of the starch, that varies with the manufacture and the quality of the raw material that you start out with.

Dr. Cathcart—I don't know whether there is or not. Different people are interested in different pasting methods; they have different methods of testing the value of the starch for their purposes. Take, for instance, in warp sizing: that is really a pasting operation. The test for that usually is simply to put on 5 per cent, 10 per cent or 15 per cent or more of size on a given yarn; then the breaking strength of that yarn is taken before and after sizing and that determines the pasting value for their purpose.

Mr. Persons—I am looking at it from the manufacturer's standpoint. How does he grade his stock as having different bodies of pasting strength?

Dr. Cathcart—In the case of thin boiling starches, for instance, we make what we call fluidity tests; that is, standard pastes are made up and tested by a purely arbitrary method, which passes these pastes through a small orifice.

Mr. Persons—But you reach a point where it won't flow.

Dr. Cathcart—And when you come to testing the pastes as such, there is a very crude way of doing that, by just simply making a paste and allowing it to solidify and comparing the different results with standards that we have arbitrarily established; if the paste conforms to the standard, it is all right; if it does not, it isn't all right.

Mr. Persons—It may vary considerably in determining it that way.

Dr. Cathcart—Yes, that is true.

I suppose we are going to get more light along that line when the use of the plastometer has been developed and is thoroughly understood. We don't understand it yet. It is a comparatively new idea. I don't know whether you are familiar with it or not, but it has to do with the relation between what you might call the fixed value and the food value of the paste. There is a certain definite ratio there that may work out to give us some way of absolutely standardizing.

Mr. Christison—I might give one suggestion on the last question: we found it very valuable in comparing starches of different shipments and different grades to suspend the starch in water and add caustic soda, which would gelatinize the starch; then you can take that thick, or fairly thick, mass and use it in an ordinary viscometer that you use for testing oil. That works very nicely.

Dr. Cathcart—That is a far more difficult operation, when you come down to fine points, than most people realize. We tested starches by making those alkaline pastes, gelatinizing with caustic soda, but these solutions must be measured most carefully, the temperatures controlled within a tenth of a degree and all that sort of thing, stop-watches employed, and the whole thing calibrated back to a master instrument. Of course, the instruments all vary and each individual instrument has its own special curve, and if a man is using instrument Number 7, that is calibrated back to the master instrument and reported on that. It is a rather difficult thing to do, if you are not doing it all the time.

Mr. Robbins—I think the Doctor could give us a little assistance perhaps if he could explain the ways in which he gives character to the sizing, to the starch after it is dried upon the fiber. We care little about the paste, so long as it is in proper physical condition to saturate the fiber, but there are other conditions than just the pasting of two fibers together, for instance, in warp sizing. It is not so much the strength of the fiber that we are looking for as a condition in which that thread will pass through the heddles of the loom and stand the friction back and forth against itself necessary to raise and lower the threads to permit the shuttle to go through. If that is rough, the threads will wear out and break and the weaving will be poor. The character that we like to have in it is something more, you might say, the difference between sizing with glass and sizing with horn. If the glass is bent a little bit, the sizing will crack and the

thread will lose its elasticity and the friction will break it, and as a result you will have poor weaving; whereas, if it dries tough, more of the character of horn, it will stand that bending and it will weave very well. The making of soluble starch doesn't seem always to do that. We want the same characteristic in finishing.

I have known a very highly soluble corn starch to size a piece of cloth very well, apparently satisfactory, but when it goes through the calender it comes out like a rag, the size being so flinty that the calender breaks it down and it loses its characteristics.

I think if we have some enlightenment upon some treatment that would make this starch paste dry upon the fiber in such a way as to be tough instead of brittle, we would be materially helped, especially in the use of corn starch, because that is the most likely to dry crystalline and harsh of any of the most popularly used starches.

Dr. Cathcart—Of course, the question of sizing warps and the question of finishing fabrics are of two different classes. If I get you correctly, what you are more particularly interested in is really the warp sizes. In the first place, in warp sizing, you want simply strength and lubrication. You get the strength from the starch and you get the lubrication from the softening of the materials that you put in in connection with the starch.

In that respect, you also have to consider the loss of elasticity. The unsized yarn, of course, is always more elastic than the sized yarn, no matter what kind of size you put on the yarn. It carries with it a certain loss of stretch or elasticity. That kind which will give you the smallest decrease of elasticity or the smallest loss of stretch will stand up better in your looms than that which will give you a larger decrease in elasticity. That point was also gone into very definitely by Mr. Hoxie, to whom I referred previously, and he established those values, which were very strongly in favor of the thin boiling starches.

I might say that that work to which I referred of Mr. Hoxie's was an entirely independent piece of investigation. Mr. Hoxie did that work at the instigation of his own interests. He did not know what kind of starches he was handling at all; it was purely accidental that it came out in the way that it did. I mean the selection was made in the manner that it was made.

As far as the finishing is concerned, the kind of feel that you get on your final piece of goods depends upon the combination of materials which you have used, whether you use soluble oils, or sulphonated oils, tallow, glycerine, mineral salts, a combination of any of the kinds of starches, or dextrin—that you can vary almost at your will.

If you attempt to finish a piece of cloth with absolutely plain starch of any kind, you will get entirely different results from what you would get if you used starch of a combination of the things that are going to give you the feel that you want on your cloth. You get a harsher feel on a piece of cloth with a starch of very high fluidity than you will with a purified starch of the alkaline type. You get a fuller feel with the latter kind of starch than you would with a starch of high fluidity. But those are modifications, and have to be adapted to the individual cases.

Mr. Chamberlain—I would like to add one more ray of light, possibly, in connection with the question the gentleman asked as to why certain starches make brittle fiber, and yarn.

There have been a great many mixtures marketed for these various special purposes. We have found what you would call a very highly soluble starch, that was a mechanical mixture of a highly converted dextrin with an ordinary thick-bodied starch of common pearl starch —in that case you would get some of the soluble advantage, but you would get all the disadvantage that comes with the harsh starching effect of straight pearl starch. For instance, take shirt fronts: in the old days when they used heavy starch, they would frequently break. Some of you older men will remember that. A shirt front laundered with the proper modified starch is flexible, very similar to the effect obtained from wheat starch. And where you make a blanket of a soluble dextrin with a thick boiling, harsh starching, natural starch, you get both effects. That has happened in our experience, and possibly that may be along the line of what you had in mind.

You do get flexible effects from the straight starch, especially when used in conjunction with the proper compound; but you get more flexible results with certain starches than you do with others, and from common pearl starch you get the least.

Mr. Robbins—Mr. Chairman, I had in mind that peculiar difference there is between corn starch and sago flour or tapioca flour or potato starch. So far, the experts haven't been able to make corn starch behave and give such a feeling to a piece of cloth as tapioca flour or sago flour gives. I was in hopes that I would get the explanation here as to what mixture of ingredients is necessary in making the size, to enable the corn starch preparation to give the same quality of feel that the other starches do, because usually corn starch is much cheaper.

Mr. Beattie—In that connection, I think probably I can add a little light: If one takes a real good corn starch and adds to it a small percentage of, say, a correctly prepared British gum, we can get just the feel we require. In our particular section of the textile industry we not only have to have weight but we have to have feel, too, and we find that if we take, say, about 75 per cent of a corn starch and the remainder of a correctly prepared British gum, we can get just the feel we re-

quire. We also use that material for back sizing. You know if you bend a carpet over, if there is anything brittle about it, it will all fly off. So that that would partly explain the question that has been put.

It is the same with the sizing of carpets. It doesn't matter whether it is linen, four-eighths cotton, jute or whether it is hemp, for instance, and particularly in the four-eighths cotton, the penetration question comes in. It isn't a question of penetration of fiber; it is a question of penetration of interstices of the individual counts in the four-eighths cotton.

Dr. Cathcart—I think, Mr. President, if I may say a word, that most of the impressions that have been formed with regard to the comparative values of corn starch as compared with other types of starches are based upon the fact that when corn starch was first offered to the textile industry, nothing but pearl starch was known. A good many opinions formed at that time have hung over, and they were so firmly formed that a great many people thought it wasn't any use to try any further. But that was the first offering the corn starch manufacturers had to give to the textile industry. These recent developments are really comparatively new to the industry.

Go back five or ten years, and you find that very few people were using thin boiling starches in the textile industry at all, and we have never found any great difficulty in getting special effects, if people were patient enough to find out exactly what could be done.

President Olney—Thank you very much.

President Olney made some announcements with regard to a photograph being taken, also with regard to registration, after which the meeting adjourned, at 12.25.

Editor's Note—The proceedings of the afternoon session will appear in the issue of January 15.

NEW MEMBERS

The following applicants were admitted to membership at the Council meeting held in Boston on December 19, 1922:

Active Membership

Alter, Frederick A., 152 Sachem Street, Norwich, Conn.
Dyer, Falls Company.

Beck, Joseph F., 2555 Cooper Avenue, Evergreen, L. I.
Textile Colorist, J. Campbell Company, New York, N. Y.

Bloxam, Harold C., 3 East Twelfth Street, Wilmington, Del.
Textile Printer and Colorist, Du Pont Company.

Bloxham, Charles W., 65 Englewood Avenue, Pawtucket, R. I.
Colorist, U. S. Finishing Company, Providence, R. I.

Davidson, E. P., 1127 West Street, Wilmington, Del.
Colorist, Du Pont Company.

Fernandez, Richard O., 9 Governors Avenue, Winchester, Mass.
Chemical Engineer, Merrimac Chemical Company.

Fitz Gibbon, R., 134 Cedar Street, New York, N. Y.
Salesman and Technical Demonstrator, Ciba Company.

Knights, Charles C., 40 Rector Street, New York, N. Y.
Assistant Resident Manager, National Aniline & Chemical Company.

Lange, Joseph S., 89 Barclay Street, New York, N. Y.
Salesman and Demonstrator, Geigy Company, Inc.

Lichtenstein, Alfred F., Box 994, City Hall Station, New York City.
Vice-President and Treasurer, Ciba Company.

Palizza, Louis, 18 Taylor Street, Pawtucket, R. I.
Boss Dyer, Home Bleach & Dye Works.

Schoedler, Dr. Ulrich, Arabol Manufacturing Company, 100 William Street, New York, N. Y.
Manager Textile Department.

Watson, Warren N., U. S. Tariff Commission, 338 O Street, Northwest, Washington, D. C.
Dye Chemist.

Junior Membership

Blauvelt, R., Newport Chemical Works, Passaic, N. J.
Colorist.

Coyle, Frank T., 442 Broad Street, Providence, R. I.
Second-Hand Dye House, U. S. Finishing Co.

Duffy, Edward J., 47 Kepler Street, Pawtucket, R. I.
Foreman Color Mixer, U. S. Finishing Company.

Goodavage, Joseph Edward, 2701 E. Westmoreland Street, Philadelphia, Pa.
Instructor Dyeing, Philadelphia Textile School.

Hacking, Arthur, 44 Melrose Avenue, Pawtucket, R. I.
Second-Hand Dye House, U. S. Finishing Company, Providence, R. I.

Hampshire, Alfred E., 61 Morris Avenue, Pawtucket, R. I.
Assistant Chemist, Glenlyon Yarn Dye Works.

Macadam, Jr., John, 2301 Grant Avenue, Wilmington, Del.
Mill Chemist, Jos. Bancroft Sons Company.

Savage, John S., 47 Seymour Street, Newark, N. J.
Dyer's Assistant, Clark Thread Company.

Stewart, William A., Laboratory, Joseph Bancroft & Sons Company, Wilmington, Del.
Textile Chemist.

Wilbur Clifford K., 14 Lexington Avenue, Eden Park, R. I.
Chemist, Cotton Finishing, U. S. Finishing Company, Providence, R. I.

DYEING WOOLEN YARN FOR KNITTED WEAR

(*Continued from page* 8.)

lutely fast dyes, for the subsequent fulling, potting and other treatments have an extraordinarily strong action on the dyeing. Not only mechanical operation is concerned here, but also a chemical treatment of the most intensive action. For such requirements, only dyes of the mordant type can be used, which must be chosen most expertly in order to stand the tests, in regard to the fastness of the original shade as also the impossibility of running into yarns which have been woven in, and are of lighter color or of white.

Of course, these textile materials, which have been dyed fast for manufacturing reasons, are when used later benefited by the fastness of the shade and enjoy a longer life. If, therefore, the dyer has absolutely full liberty in the selection of the dyes for woolen yarn used in knitted wearing apparel, and if he, without incurring any danger, can use the simplest and cheapest colors, the acid dyes, he will be somewhat restricted in the selection of the available dyes when deciding by what process he shall dye so that the colors of the knitted apparel do not fade too quickly.

Fastness to Light Requirements

As knitted garments are usually worn in the open as outer garments, and consequently the colors are often exposed to the light, frequently to the direct rays of the sun, it is an essential condition that the dyer should use colors as fast to light as possible. It is true, there are but few dyes which are sufficiently fast to light that they are absolutely resistant to the direct rays of the sun, but there are dyes which are fast even when exposed for a long time to the light of day, and may, therefore, be called fast to light and used accordingly.

It has often caused surprise in regard to old rugs that the colors have retained their brightness for such an interminable length of time; but this is not due to the fact that they have any special resistance to light, but can be traced to the manner in which they are kept, as the light is usually excluded from them, making it almost impossible even for colors which in direct sunlight would fade in a few days to lose their color and luster. We are able to-day not only to dye fast to light, but many shades can be made even more fast to light than formerly.

The process of dyeing colors fast to light is possible with all dark and also with all full and deep shades, with many dyes. It is not necessary to choose dyes which are particularly fast to light, for even those of moderate fastness produce good results in dyeing, for the reason that the greater quantity of dye on the fiber guarantees a certain degree of fastness to light. For medium shades also there is adequate selection.

The dyer is restricted in the selection of the dye if the shade is to be light and vivid, as quite a number of these shades cannot be dyed fast to light at all, for the reason that the dyer is compelled to take the dyes for this purpose from specific groups lacking fastness to light. Anybody who is determined to wear clothing so colored must not grumble when the colors fade. In the course of the last decade the dye factories constantly increased the number of dyes manufactured in bright and light tones which were fast to light, so that to-day many such shades can be produced successfully.

Alizarines

These colors are acid alizarine and extra concentrated alizarine dyes, and are practically indispensable. Generally speaking, they can be dyed in the customary acid bath and can, as a rule, be used with the ordinary acid wool dyes. Stress should also be put on the good leveling property which they possess, making it possible to use them for mixed dyeings and for cross-dyeing. The dyer is only restricted in their use by their comparatively small yield, particularly in regard to the extra alizarine dyes, and by the very high price.

These dyes are also often used as admixtures with other poorer but cheaper dyes of the same or similar shade, so that in this way dyeings can be produced which are not too expensive and are, nevertheless, fast to light.

It is a well-known fact that dyeing establishments use alizarine dyes very largely in order to be able to dye carpets and furniture coverings fast to light. Special expert knowledge is necessary to select the dyes for mixed colors. We refer not only to the varied colors known as mode shades, but to all the colors which cannot be dyed with one dye only; that is therefore, as almost every expert knows, most colors which are produced. In the selection of the various dyes a mixture of which is to give the desired shade, it is of the greatest importance that this selection be made in such a manner that when the finished shade is exposed to light it slowly fades in the same shade. Consequently, there must never be any dyes in the mixture which are faster than the other dyes used, as they would predominate and would cause a great change in the tone of the original color.

As with increasing quantity of dye on the fiber its lightproof quality is greatly improved, this must, under given circumstances, be partially or entirely replaced by one not as lightproof in order to obtain a mixed color which fades properly in the same tone. On the other hand, when a small quantity is required a dye must, of course, be used which is particularly fast to light. Alizarine rubinol, when used in small quantities in mixed colors, is exceedingly favorable; when, however, more red dye is required, it is much too fast to light as compared with the other component substances, and therefore is replaced either partially or

entirely by a less excellent dye that must be indicated by tests. On the other hand, the toning dyes, which are only required in small amounts, must be very fast to light in order to be as fast in the dyeing as the main dye used, the quantity of which is many times that of the former.

Attention should be called to the fact that, in addition to dyes whose colors fade in the light to the same shade but of different tone, there are also dyes the color of which is materially changed when subject to light. When these are used in mixed shades the result should be tested. Although it requires a great deal of effort and time to control the fastness of every new dye used, the conscientious dyer will do this and will not be satisfied with inadequate testing of the individual dyes. Within a very short time the effort expended will be rewarded.

Fast and Bright Shades

First of all, we are concerned with the production of bright tints ordinarily obtained with the basic dyes. Their use for knittings must be entirely excluded, as they have not the least claim to fastness to light. Anybody who insists on having rhodamine colors must be satisfied with their want of fastness to light. Acid magenta gives a less original shade but is sufficiently fast to light.

The same is true in regard to the inferior qualities of bright, light blue and alkali blue shades. These would have to be dyed with the various brands of alkali blue or Victoria blue, which are very fugitive to light. Unfortunately, fast colors cannot be obtained with the vivid brilliant wool blue and brilliant fulling blue, which are dyed in the acid bath. By the addition of Alizarine Uranol R or 2B, which is not quite as bright, the resistance to light can be greatly improved. In order to obtain level dyeings, however, the dyeing must be done carefully. For a light blue shade not quite as vivid, Alizarine Sapphirol, Alizarine Direct Blue, Cynanthrol, Anthraglaucol, Anthrazine, Anthracyanine, Acidolcyanine can be used, according to the shade desired. With all these the dyeing can be done in the ordinary acid bath, no special precaution being required, as these dyes level well. Furthermore, attention is particularly directed for these purposes to Alizarine Pure Blue B and Alizarine Direct Blue B, dyes that have a strong resistance to light. These must be dyed in a weak acid bath, preferably with acetic acid, in order to obtain uniform colors. If necessary, the colors obtained with the above products can be made more vivid by a small addition of brilliant wool blue. At all events, the utilization of patent blue and acid purple, formerly very popular, must be given up, as they are very fugitive to light.

The very popular shades of cornflower blue, azure blue and others which are vivid, full blue shades for knitted sweaters and jackets are also dyed with the above dyes and given a good luster by the addition of brilliant wool blue. By toning with fast acid purple, azo acid purple, or even with pure red leveling dyes, shades with a reddish cast are obtained. Blue shades with a greenish cast, like peacock blue, are also obtained with the above dyes and, if desired, can be toned somewhat with acid green, patent blue and light fast yellow. Attention is called, for these purposes, to the cheap and very excellent Anthracyanine, and, furthermore, most particularly to Alizarine Astrol, which is very fast to light, levels well and can, therefore, be recommended particularly for lighter greenish cast blue tones.

The very vivid, light greenish cast turquoise-blue tones known are welcomed for knitted sweaters, and these can only be obtained with the various brands of patent blue and brilliant acid blue. However, the fact remains that these dyes, even in full shades, are not very fast to light.

Navy blue and dark blue are mostly dyed from a mixture of blue, purple, green, yellow, orange and red Some dyers mix colors themselves; others resort to finished mixed products. Victoria navy blue, naphthalene blue, acidol navy blue, acid purple, Victoria purple, ethyl acid purple, naphthalene green, alkali fast green are all used. By the addition of anthracyanine the resistance to light can be improved. Wool fast blue in full shades is also very good. For dark blue, the sulphocyanines and alphanol blue are important: it is a well-known fact that these dyes must be dyed with great care, preferably with ammonium acetate, beginning at a low temperature and gradually rising in order to obtain uniform colors.

Vivid light green shades cannot be dyed fast to light, nor the fuller shades such as Paris green and sea green. Acid green and naphthalene green may be used, also patent blue, brilliant acid blue toned with flavazine, and light fast yellow. In case of the less vivid shades, by the addition of anthracyanine green, anthraquinone green or alizarine saphirol, alizarine astrol and yellow, the resistance to light can be improved. With the same dyes, medium and dark greens are dyed and made darker with purple or red leveling dyes. If cost permits, the somewhat more expensive alizarine saphirol, alizarine direct blue, alizarine astrol and yellow may be used with the addition of as much patent blue as is necessary to fill the shade.

Resistance to Rubbing

These dyes have, further, the advantage of greater resistance to rubbing as compared with results obtained by dyeing with naphthalene green and others which easily rub off or crock, especially in full shades. The dyer of woolen yarns is wise to pay attention to the production of colors which do not rub, as the knitted wear is frequently worn over light colored apparel.

Olives and Browns

For olive, leather brown, Havana, dark brown, the usual leveling dyes, such as alizarine direct blue, alizarine saphirol, cyanathrol with tartrazine, flavazine, light fast yellow, guinea yellow, and for red azophloxine amino red wool fast red, azo fuchsine can be used. Alizarine astrol, supramine yellow, supramine red are very good. These dyes are somewhat more expensive, but yield very much better results than the former. When dyeing with these dyes, the addition of acid must be restricted to a small quantity and must be carefully done, and the bath must also be held at the boiling point long enough in order to produce uniform results. Of course, any necessary additions to obtain the desired shade are best effected with leveling dyes. After short practice these dyes are used without any difficulty. Although of no interest in connection with knitted apparel, it should be mentioned that the supramine dyes yield good colors fast to washing.

Yellow is dyed with flavazine, light fast yellow, tartrazine, anthra yellow, wool fast yellow, guinea fast yellow; supramine yellow is also very popular, owing to its greater fastness. Some dyeing establishments also use direct dyes, such as chrysophenine, fulling yellow, sulphon yellow.

Orange, tango, copper, gold are produced with the above yellow dyes, with the addition of red or blue leveling dyes. Supramine yellow also, with supramine red, as also sulphon orange and milling orange, is used. As a large quantity of dye is necessary for these shades. this guarantees up to a certain point good resistance to light, so that there is not very much restriction in the choice of dyes.

Reds

The red shades, which were formerly very much in vogue but which are now unpopular for knitted wear, such as scarlet, cardinal red, madder red, should be mentioned. As hitherto, they have always been dyed with ponceau, crocein, fast red and naphthol red, but somewhat more fast with milling red, benzole scarlet, diamine scarlet, diamine fast red and benzo fast red.

Lighter red shades, such as coral, strawberry and peach, are dyed with level dyeing red dyes of good resistance to light, such as amino red, wool fast red, anthrarubine, and especially, owing to the small quantity of dye necessary, with the excellent light fast alizarine rubinol.

For cherry red, carmine, wine red and ruby red, there are a large number of good dyes with which very vivid and fast to light dyeings can be obtained: azophloxine, fast acid red, anthrarubine, guinea fast red, azofuchsine, amine red, wool fast red, acid fast purple, azo acid purple, and also alizarine rubinol, alizarine geranol, alizarine irisol, alizarine direct purple, alizarine cyanole purple and anthraviol, the latter being especially suitable for toning owing to its excellent resistance to light. It is obvious that the old brands of acid purple are entirely excluded, for their use as a toning dye for ruby red would be entirely incorrect, as the requisite small quantity of purple dye on the fiber would fade particularly quickly; that is, there would be a decided change of the original color after having been worn a few days in the open daylight.

For purple and lilac shades, the old acid purple dyes offer a large selection of vivid and satisfactory tones. But they themselves should only be used for full shades, owing to their fugitiveness to light. If at all possible it would be preferable to produce somewhat duller shades with alizarine direct purple, alizarine irisol, anthraquinone purple and anthraviol. These could be toned in the less fast to light dyes to save expense.

The large number of mode shades (including gray) are, of course, dyed with dyes possessing the best lightproof and leveling properties. In these various shades the dyer should be particularly careful to ascertain by exposure tests whether the color will fade and to determine what dye should be added to the mixture to give the proper results. It is entirely impossible to give detailed information in this regard. The most important dyes for mode shades are alizarine saphirol, cyananthrol, alizarine direct blue and anthraglaucol, also wool fast red, amino red, azophloxine, alizarine rubinol and flavazine, tartrazine light fast yellow, guinea fast yellow and anthra yellow. For the sake of completeness the dyeing of black and the production of white will be described.

Dyeing Black

To dye wool yarn black for knitted apparel, the naphthylamine blacks which are simply dyed with sulphuric acid are sufficient. Some among these are satisfactorily fast to light brands. Better, however, are the somewhat faster black dyes, such as nerol, nerocyanine, sulphoncyanine black, alphanol black, neotolyl black and also the somewhat cheaper sulphon acid black. They are dyed with acetic acid, but are somewhat cheaper dyed with formic acid, and also no special precautions are necessary. The production of a particularly deep black by the use of a high percentage of black dye should be avoided on account of the expense, and also on account of bad resistance to rubbing. A sufficiently deep black can be obtained by the addition of yellow or orange.

The best white on woolen yarn is obtained by bleaching in a peroxide of hydrogen bath. This is best prepared by adding sodium peroxide to the bleaching water, to which sulphuric acid has been added. If the yarn after the hydrogen peroxide bath is stoved, the white is improved. Particularly yellow wool must be blued.

To obtain a good, uniform, spotless and rub fast

dyeing, the yarn must be thoroughly cleaned and free from fat. The dyer should inspect the yarn and should not be stopped by the expense of cleaning, for in the long run it will pay well.

We have shown that an extremely large number of dyes are available. For full and dark tones, therefore, the customary cheap acid dyes are used; for light, as also for mixed, shades, the light fast leveling dyes, and the latter are also used for toning, as also for subsequent dyeing. The bath should not be started too hot, in order to avoid irregular dyeing. Most of these dyes can be used with sulphuric acid from 2 to 4 per cent. The woolen yarn dyer prefers acid sodium sulphate to sulphuric acid. About three times as much of it is to be taken as of the acid. Acid sodium sulphate is somewhat milder in its action and assures, therefore, a slower and more uniform absorption of the dye on the fiber. A standing bath is advantageous, not only on account of the economy of steam and acid effected but because in the old dye liquors more uniform and sometimes purer shades are obtained. When starting a new dye liquor with fresh water, therefore, usually a part, to be dyed black later, is first boiled with the addition of acid, and only then, in this now old bath, the lots to be dyed are started. With dyes to which weaker acids must be added, acetic acid must be used or the very much cheaper formic acid. As the latter is very much more acid, when measuring the quantities to be added the greatest care must be exercised. If dyes are mixed part of which are to be used with acetic acid or formic acid, and the other part in a strongly acid bath, dyeing is started with acetic acid or formic acid, and the sulphuric acid is added later. However, in such cases the mineral acid can often be substituted by the addition of further quantities of the formic acid, which has a strongly acid action.

This manner of procedure also has the advantage that the bath can always be used again for the next dyeing, the new bath being started without the addition of any acid.

Apparatus Dyeing

Large quantities of wool yarn are still being dyed in becks and turned by hand. The adherence to tradition or the desire to utilize further the equipment in existence causes many dyers to follow this old procedure; nevertheless, a very decided change of shade in various lots or a decided difference in the size of the various lots will make it appear desirable to give the preference to hand dyeing. However, where many large lots must be dyed, and where they are almost all to be dyed in the same or similar shades, machines or apparatus must be used. The old dyeing apparatus which presses the fabric strongly together is very seldom used. It has been superseded by machines of the Obermaier type. Whereas in the pack system the hanks are stationary and the dye liquor is forced through by means of a propeller or pump, in the Obermaier machine the dye liquor remains stationary and the yarn is moved in a simple manner up and down in the bath. Even the smallest lots can be dyed.

In all these systems woolen yarn is dyed in large quantities with perfect results. In black and colors, very uniform and spotless results are obtained. After a short period of time necessary to accustom oneself to the process, a large sum is saved in wages and steam; for, generally speaking, one attendant on the machine accomplishes as much as three hand workers. The same favorable ratio holds true of the consumption of steam, so that initial cost of this apparatus is covered very soon. Furthermore, in machine dyeing, if a proper process of dyeing is followed, perfect lots are obtained invariably; and this is not always the case by hand, if for no other reason than owing to irregular turning. Furthermore, attention must be called to the fact that the wool yarn dyed in apparatus remains smoother and does not tangle as is the case with hand work. It can be wound much better and more quickly, and results in very much less waste; which is an important factor.

Necessity of Softened Water

Whereas the dyer working at the beck is accustomed to add the necessary quantity of acid in several portions, the dyer working at a machine has his special attention called to the fact that in order to obtain uniform colors the total quantity of acid required is best added at the beginning; dyeing is started at a low temperature and the bath is slowly heated. Subsequent additions of acid into the hot dye liquor would cause a sudden irregular adsorption of the remaining dye.

For the good results it is absolutely essential that the dye containers contain no iron parts inside, for most dyes are susceptible to iron. Even copper or bronze is injurious to many colors; it has a neutralizing action, particularly in those parts which come in constant contact with it during the dyeing. Ammonium thiocyanate, which is recommended as a preventive, does not help sufficiently as a general rule. The becks must, therefore, be of wood and contain only metal parts that are absolutely essential, such as steam pipe, certain machine parts, such as fittings. The manufacturers of dyeing apparatus and machines have acted accordingly to the fullest extent. It should also be mentioned that the steam pipe is provided with steam discharge outlets in such a manner that a uniform heating and uniform mild boiling is possible. The yarn dyeing apparatus has special heating spaces; this is necessary, because in stationary dyeing part of the hanks would be in close proximity to the heating pipe.

The Obermaier machine with movable dyeing material can be heated, similarly to the beck, directly by means of an inserted steam coil, for as a result of the motion in both cases the hanks would again and again be moved away from the proximity of the heating body.—Texilberichte, through Dyer & Calico Printer.

Catalysts in Bleaching and Dyeing

Effect of Vanadium—Influence of Light and Air—Action of Copper Oxide—Catalysts in Dyeing Aniline Black—Developed Colors

By A. J. HALL

IN these days when most people are familiar with the well-known industrial process in which sulphur dioxide is converted into sulphuric acid by means of platinized asbestos, and the hardening of liquid oils with hydrogen in the presence of finely divided nickel, a definition of what a catalyst is may almost be omitted. More enlightening than a definition is a pretty experiment involving a curious property of oxycellulose which was first performed some forty years ago.

Effect of Vanadium

At that time a Continental bleaching and dyeing works was seriously troubled with faulty bleaching. As chemist, Witz thoroughly investigated the matter, and as a result several interesting facts concerning bleaching were revealed. Among these Witz showed that if a piece of oxycellulose was immersed in a solution containing as little as 0.00000001 gram of vanadium per liter, the vanadium became absorbed by the fabric, and that if this was then padded with a solution containing aniline hydrochloride and an oxidizing agent and subsequently aged, aniline black was formed. Under the same conditions fabric containing no oxycellulose failed to develop an aniline black shade. In this experiment it is, of course, the excessively small quantity of vanadium absorbed by the fabric which is able to cause catalytically the oxidation of the aniline.

In bleaching and dyeing there are numerous instances of catalytic action—sometimes a harmful action. Particularly noticeable is the ease with which cellulose can be catalytically converted into hydrocellulose and oxycellulose—substances which most bleachers seldom wish to meet with.

For instance, in Witz's investigations, as referred to above, it was soon found that bleaching liquors were affected by light and metallic compounds. In some instances the faultily bleached fabrics actually contained holes, these being due sometimes to excessively strong bleach liquor, and in other cases to impurities present in the cloth which induced the bleach liquor to act with abnormal energy.

Influence of Light and Air

In one experiment Witz suspended a piece of cotton fabric so that part of it was immersed in a bleach liquor while the remaining portion was exposed to light and air. After a suitable period had elapsed the fabric was well washed and then immersed in a weak solution of Methylene Blue. It was then seen that while the portion which had been immersed in the bleach liquor had but a slight affinity for this dye, a strong blue band marked the point at which the fabric had just been immersed, and a fairly dark blue shade characterized the exposed portion. That is, the bleach liquor which had risen by capillary attraction into the exposed portion of the fabric had transformed under the combined action of light and air, the cellulose to oxycellulose.

This influence of light on fabric which has been padded with a bleach liquor is very marked. Hence in bleaching lowed to lie in piles, it is particularly necessary to protect the fabric from direct sunlight. Failure to do this may result in the formation of oxycellulose stains.

The effect of air on bleach liquors is probably something more than catalytic. The carbon dioxide which air always contains is chiefly responsible for the increased activity of a solution of bleaching powders through which air has been bubbled.

It is generally recognized that an alkaline bleach liquor is less active than one which has been acidified. Carbon dioxide is feebly acid. Hence, when a bleach liquor absorbs this gas, it becomes less alkaline and therefore more reactive.

This activating effect of carbon dioxide has long been known. At first attempts were made to utilize this action, and bleaching processes were devised in which the cloth padded with bleach liquor was subjected to the action of carbon dioxide. But it is doubtful whether such processes are used at the present time, since the bleaching can be controlled more easily by other methods.

The catalytic effect of metallic stains are also seriously felt in bleaching. Frequently fabric are found to have weak patches after bleaching, and these can sometimes be traced to the presence of oil stains containing iron oxide (rust) in the unbleached fabric. In general, most metals increase the activity of bleach liquors, but copper and iron are particularly effective in this respect. In this connection some interesting experiments have been carried out by Kind.

It was found, for example, that on standing for about twenty-four hours a feebly alkaline bleach liquor lost 4.2 per cent in strength. To samples of similar bleach liquors equal quantities of copper oxide, powdered copper, iron oxide and powdered iron were added and allowed to stand twenty-four hours. It was then found that the losses of strength which occurred were 79.2 per cent, 18.1 per cent, 29.2 per cent, and 5.6 per cent respectively.

Action of Copper Oxide

The catalytic action of copper oxide is especially noticeable, in spite of the fact that the bleach liquor was dis-

tinctly alkaline. With feebly acid bleach liquors the catalytic effect was even greater.

Samples of fabric to which were attached pieces of metal were also immersed in similar bleach liquors. It was found that the strength of the sample having iron attached to it was much inferior to that of the sample having copper attached. Both of these samples, however, had less strength than one not in contact with a metal.

Curiously enough, these metals also render solutions of hydrogen peroxide, sodium peroxide and sodium perborate considerably less stable, and therefore more reactive. Hence when bleaching is carried out by means of these reagents, wooden vessels should preferably be employed. A point worthy of notice, however, is that the addition of sodium silicate to such solutions partly neutralizes the catalytic effect of metallic impurities.

In the keiring of cotton fabrics catalytic action often results in the formation of oxycellulose. Cellulose containing a hot alkaline liquor does not readily oxidize when exposed to the air. If, however, under similar conditions the cellulose is in contact with metallic substances oxidation occurs more readily.

While dealing with bleaching mention might here be made of an improved process recently patented by the Zellstoff-Fabrik, Mannheim-Waldhof. It seems quite probable that its increased efficiency of bleaching is partly due to catalytic action. The process was first devised for the bleaching of wood pulp, but Ristenpart has now tested it as a process for cotton fabrics.

The essential feature of this process consists in treating the fabric first with an acid and then with an alkaline bleach liquor. The results obtained are quite superior to those produced by means of an acid or an alkaline bleach liquor alone. Ristenpart thus found that by use of acid and alkaline bleach liquors each containing one-third gram of active chlorine per liter, cotton fabric was equally as well bleached yet with less loss of strength as when an ordinary bleach liquor containing two grams of chlorine per liter was used. The process allows a considerable saving of time and of bleaching powder, and is not attended with the formation of oxycellulose.

Finally, a curious formation of oxycellulose has been mentioned by Knecht. He immersed two samples of cotton fabric, one of which was mordanted with chromium, in an alkaline solution containing 3 per cent of hydrogen peroxide. Under these conditions the chromium is converted into sodium chromate which, being soluble, leaves the fabric and passes into solution. Knecht found that under these circumstances the mordanted fabric became tender while the unmordanted remained strong. Thus instead of the chromium protecting the cellulose, it catalytically hastened its oxidation to oxycellulose.

Catalysts in Dyeing

In dyeing and printing the use of catalysts is well known. The dyeing of aniline black and the use of anthraquinone as a catalyst in the hydrosulphite discharge of certain ice colors will at once be recalled.

When a discharge paste containing a formaldehyde-sulphoxylate compound is printed on a fabric dyed with para red, and this is then steamed, a satisfactory white discharge is obtained. In the case of alpha-naphtylamine claret and similar shades obtained by means of benzidene and tolidine, the discharge is more difficult. However, this difficulty is now overcome by adding various catalysts to the discharge paste.

Thus Meister Lucius and Bruning early discovered that certain formaldehyde compounds of ortho and para-toluidine, xylidine, etc., were useful catalysts. Later, the B. A. S. F. found that Induline Scarlet was much more effective for this purpose. Instead of Induline Scarlet other dyes such as Methylene Blue, Patent Blue, Rhodamine and Alizarin Orange may be used, but they are less effective. Finally, Sunder discovered another suitable catalyst in the substance anthraquinone. It is very satisfactory, and has the advantage that it does not tinge the white discharges produced. Anthraquinone is largely used for this purpose.

Aniline Black

Aniline black dyeing has been the subject of so many researches and patent lawsuits that it is not surprising that a large amount of knowledge concerning it is available. Essentially it is a catalytic reaction. Nearly all aniline black processes which are utilized depend on the fact that a mixture containing aniline salt and an oxidant readily react in the presence of a metal such as iron, copper, chromium and vanadium. As has been previously pointed out, vanadium is a particularly effective catalyst.

In the prussiate aniline black process sodium ferricyanide is the catalyst used. It is, however, somewhat difficult to say whether the action of this substance is entirely catalytic. Theoretically, in the formation of the black, the sodium ferrocyanide accepts oxygen from the sodium chlorate used and thereby changes to sodium ferrocyanide. This immediately passes its oxygen to the aniline, thereby becoming reduced to the ferrocyanide once more. But against this must be placed the fact that in the formation of the aniline black a considerable portion of prussiate is destroyed, and this must necessarily have something more than a catalytic effect.

The most interesting catalyst in aniline black dyeing, however, is paraphenylene diamine. This substance undoubtedly assists the oxidation of aniline to a remarkable extent. Green, who investigated this action, has, of course, patented the process, and it is strange that so promising a method should not now be employed.

Many aniline black dyers add turpentine to the padding liquor. The reason for this is to be found in the fact that turpentine is capable of auto-oxidation. That is, it is able to render oxygen more active—probably through formation of ozone. Hence, in the padding liquor, there is the possibility that the turpentine will hasten the oxidation of the aniline.

In the dyeing of ingrain colors it is interesting to recall the experience of Green, who discovered Primuline, as showing the catalytic effect of sunlight on diazo compounds. Green has recorded himself that shortly after his discovery that Primuline could be diazotized and coupled with beta-naphthol and similar compounds with formation of fast pigment dyes, he visited several dyehouses for the purpose of demonstrating his discovery. On one occasion fabrics which had been padded with diazotized Primuline in the usual manner and had then been placed through a developing bath containing beta-naphthol came up very patchy. This was investigated and found to be due to the fact that the fabric, before development, had been exposed to sunlight—Dyer & Calico Printer.

Sulphur Dyes Prepared from Xylan

Nature and Preparation of Xylan—Supply Adequate—A Black and a Blue Dye Thus Far Prepared—Dyes from Xylan and Nitro Products

By ELTON RICHMOND DARLING and ROBERT ELLIS ARMSTRONG

MANY products have in the past been used for the manufacture of sulphur dyes. The employment of xylan, or wood gum, adds one more to the list, and this may be accorded a place among the more successful ones.

Xylan, or wood gum, is a product that can be obtained from wood and other ligno materials in small quantities. But in the corncob it occurs in such quantities as to make it profitable to extract it for commercial purposes. The amount of raw material, especially in the corn producing States, is enormous, and no scarcity would result for a long time. The red cob seems to furnish a more satisfactory product than does the yellow cob. This may be due to the coloring matter present in the cob which is carried with it through the process.

Preparing the Xylan

The coarsely ground corncobs are first well covered with a 3 per cent solution of caustic soda and heated under ten pounds pressure for one hour in an autoclave. The resulting mass is then filtered and the residue given a slight wash. The resulting liquors are all united, giving a dark brown solution. To this is added dilute sulphuric acid until there is present an excess amount to about 2 per cent. By this treatment a brown insoluble product is obtained which is filtered off. This is then taken and added to a hot 5 per cent solution of sulphuric acid, which converts it into a dark brown brittle mass. This product is well washed with water and dried, upon which it is reduced to a fine powder by grinding. The yield from the cob by this treatment is high and the expense involved is low.

Preparing a Black Dye

Thus far in the work but two dyes have been prepared —one a black and the other a blue. These have been given the usual tests and compare very favorably with similar colors to be found on the market.

The black dye was the first to be prepared. Two hundred grams of the powdered xylan was taken and to this was added 825 grams of sodium sulphide and 270 grams of sulphur. To the whole was added sufficient water to give a solution, which was slowly heated until the contents of the container was a paste. This was then placed in an oven and the heating continued until a temperature of 190 deg. Cent. was obtained. The heating was continued at this temperature for six hours. At the end of this time the mass was thrown into water and made into a solution, after which dilute sulphuric acid was added to precipitate the dye. When the precipitation was complete the whole was filtered and washed free from acid. The dye was then allowed to dry.

Preparation of the Blue Base

In the preparation of the blue dye the base was first treated with nitric acid. This was carried out by adding the powdered xylan to 50 per cent solution of nitric acid. In a few minutes action started, which resulted in the evolution of dense fumes of the oxides of nitrogen. When this had ceased the xylan had changed from a dark brown to a light yellow. The whole was then filtered, washed, and at once used as in the preparation of the black dye.

Dyes from Xylan and Nitro Compounds

The black dye is obtained in the form of a dark gray to black powder. In order to improve the shade and cut down the amount of dye required to produce deep shade it was found of advantage to add to the mixture before fusion certain nitro compounds. Amounts of these materials used averaged from 10 to 20 per cent of the amount of the xylan taken.

It was further noticed that in making the dyeings it was not necessary to use the afterbath of oil to obtain a good color.

Further work is under way in an attempt to obtain other colors with this material.

The Physical Chemistry of Dyeing. Acid and Basic Dyes

Part II, Conclusion

By T. R. BRIGGS and ARTHUR W. BULL

A thesis submitted by Arthur W. Bull to the Faculty of the Graduate School of Cornell University in partial fulfillment of the requirements for the degree of Ph.D. Published in the Journal of Physical Chemistry, Ithaca, N. Y.

These curves and data show that Croceine Orange unquestionably diminishes the adsorption of hydrochloric acid by wool. Croceine Orange is a monobasic salt with the formula: $C_6H_5N:NC_{10}H_5OH(SO_3Na)$ with 6.567 per cent sodium. In this case the calculated values for the total possible amount of hydrochloric acid neutralized by the sodium in the dye agree quite well with the experimental values. It is thus apparent that Croceine Orange is adsorbed by wool largely as the free dye acid. It should be observed that these calculations are based on the assumption that any decrease in chlorine ion concentration is due only to adsorption of hydrochloric acid. It is possible, of course, that the decrease may be caused

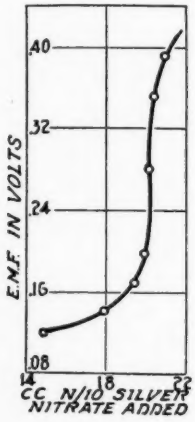


FIG. 3—*Typical curve obtained in the electrometric titration of 20 c.c. N/10 NaCl. (A saturated calomel electrode was used for the other half of the cell.)*

by adsorption of sodium chloride. Experiments were performed to determine whether this was actually the case and no adsorption of sodium chloride by wool could be detected.

Adsorption of Acid Dyes and pH of Dye Bath. Addition Agents.—The next step in the development of the general problem was to determine quantitatively the relation between the hydrogen ion concentration of the dye bath and the adsorption of various acid dyes by wool and from this to proceed to the quantitative determination of the effect of various addition agents.

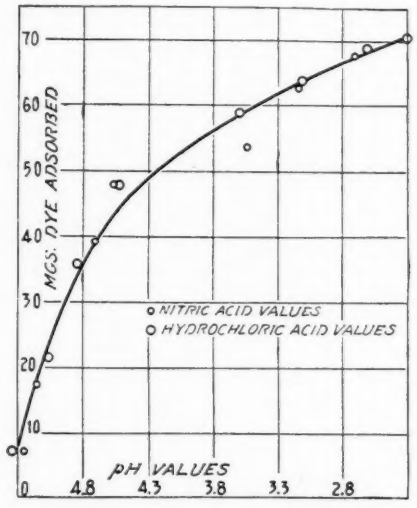


FIG. 5—*Adsorption of Croceine Orange by Wool. (Note: Fig. 4 appeared in the preceding instalment.)*

Using nitric and hydrochloric acids, two series of experiments were made on Croceine Orange to determine the relation between pH and the amount of dye adsorbed. One gram of wool was boiled for forty-five minutes in a bath containing seventy-five milligrams of dye in a total volume of 250 cc. The results are given in Table VI and in *Fig.* 5.

TABLE VI

pH AND ADSORPTION OF CROCEINE ORANGE

cc. N/10 HCl Added	Final pH	Mgs. Dye Adsorbed	cc. N/10 HNO_3 Added	Final pH	Mgs. Dye Adsorbed
0.0	5.91	4.0	...	...	...
0.5	5.35	7.0	0.5	5.25	7.0
1.0	5.07	21.4	1.0	5.15	17.2
1.5	4.85	35.7	1.5	4.72	39.1
2.0	4.53	47.8	2.0	4.55	47.9
3.0	3.60	58.9	3.0	3.53	53.6
4.0	3.12	63.5	4.0	3.13	62.5
8.0	2.61	68.8	8.0	2.70	67.7
15.0	2.30	70.4	15.0	2.32	70.1

This curve shows that the amount of Croceine Orange adsorbed by wool increases as the hydrogen ion concentration is made greater. The fact that the chloride and nitrate ions have no specific effect may be accounted for by the assumption that they are either not adsorbed or that they are adsorbed equally.

To show that a change in hydrogen ion concentration produces a similar effect on the adsorption of other acid dyes, experiments were performed using Lake Scarlet R. The experimental conditions were kept the same as those used with Croceine Orange, except that the colorimetric method was abandoned and the amount of dye remaining in the baths was determined by titration with titanium chloride. Curve (a) of *Fig.* 6 represents the data obtained (Table VII).

It is apparent that over a considerable range, the amount of Lake Scarlet R adsorbed by wool is directly proportional to the hydrogen ion concentration of the bath. As the total amount of dye in solution was only seventy-five milligrams, it is obvious that this is a limiting value which accounts for the sudden upward bend in the curve, since this upward bend represents practically

TABLE VII

pH AND ADSORPTION OF LAKE SCARLET R

cc. N/10 HCl Added	Final pH	Mgs. Dye Adsorbed
0.0	6.43	0.6
0.5	5.53	10.2
1.0	4.90	25.6
1.5	4.31	39.9
2.0	3.88	51.3
3.0	3.37	68.0
5.0	2.85	73.9
8.0	2.57	74.4
15.0	2.13	74.8

complete removal of the dye. If more dye had been used, it is probable that the proportionality between adsorption and pH would have continued over a still greater range.

In accordance with the theory of dyeing previously outlined in the introduction to this paper, the addition to the dye bath of substances forming strongly adsorbed anions will cause a decrease in the adsorption of an acid dye, and in general the greater the valence of the added anion, the greater will be its restraining action. The substitution of sulphuric or phosphoric acid for hydrochloric acid should therefore cut down the adsorption of acid dyes. A similar effect should be obtained if salts such as sodium sulphate, sodium phosphate or even sodium chloride are added to dye baths containing hydrochloric acid.

Pelet-Jolivet,[21] Lake,[22] and others have investigated this point and have shown that the addition of sulphate and phosphate does actually decrease the amount of dye adsorbed by wool. But none of these investigators were careful to allow for the change in pH of the dye bath which the added salt might produce. The results already presented in this paper make it evident that a quantitative determination of the relative and absolute effect of re-

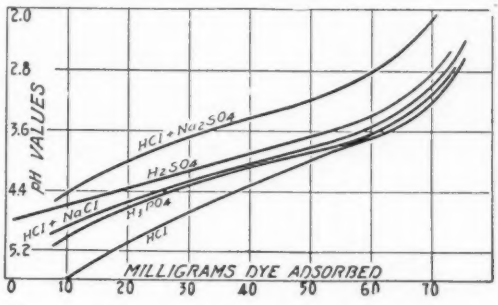


FIG. 6—*Effect of anions on the adsorption of Lake Scarlet R*

strainers such as chloride, sulphate, and phosphate can only be made in dye baths of equal hydrogen ion concentrations.

Data were therefore obtained to determine the action of restrainers on Lake Scarlet R. The experimental conditions were those described in the previous work, the dye baths (250 cc.) each containing seventy-five milligrams of dye plus different amounts of other reagents as denoted in the table of data (Table VIII). The final pH of each dye bath was ascertained as before and the amount of dye taken up by wool was determined. Curves were then drawn between pH and milligrams of dye adsorbed in the presence of the different addition agents. (Curves b, c, d, and e of *Fig.* 6.)

An inspection of these curves brings out several interesting points. The amount of dye adsorbed always increases with the hydrogen ion concentration of the bath. In order to determine the relative effect of the different addition agents, it is essential that comparisons be made at equal values of pH. This is done readily by finding where the curves cross a line parallel to the X axis representing the desired pH. Thus at a pH of 4.0, the amount of dye adsorbed in the presence of hydrochloric acid was 48 mg., in the presence of phosphoric acid, 46.5 mg., and

TABLE VIII

THE EFFECT OF ADDITION AGENTS ON THE ADSORPTION OF LAKE SCARLET R

cc. N/10 H_2SO_4	Final pH	Mgs. Dye Adsorbed
0.5	4.81	1.3
1.0	4.40	10.6
1.5	4.13	28.1
2.0	3.84	40.9
2.8	3.50	57.5
4.5	3.14	65.8
cc. N/10 H_3PO_4	Final pH	Mgs. Dye Adsorbed
1.2	4.98	10.8
2.5	4.55	22.6
4.2	4.25	39.0
5.5	3.93	48.6
7.0	3.62	57.8
8.8	3.45	64.6
12.5	3.77	68.7
20.0	2.75	73.9

cc. N/10 HCl	cc. N/10 NaCl	Final pH	Mgs. Dye Adsorbed
0.5	25.00	4.90	10.0
1.0	25.00	4.55	20.9
1.5	25.00	4.15	35.7
2.2	25.00	3.77	49.1
3.3	25.00	3.28	65.9
5.0	25.00	3.00	69.1
8.0	25.00	2.68	71.6
cc. N/10 HCl	cc. N/10 $NaSO_4$	Final pH	Mgs. Dye Adsorbed
0.5	25.00	4.55	8.6
1.0	25.00	4.05	18.9
1.5	25.00	3.80	27.9
2.0	25.00	3.80	31.0
3.0	25.00	3.36	44.0
5.0	25.00	2.88	54.5
8.0	25.00	2.70	62.0
15.0	25.00	2.37	68.5
25.0	25.00	2.07	73.1

in the presence of sulphuric acid, 30 mg., the order of dye adsorption being HCl > H_3PO_4 > H_2SO_4.

These results are in agreement with the theory. The strongly adsorbed divalent sulphate anion would be expected to cut down the amount of dye anion adsorbed.

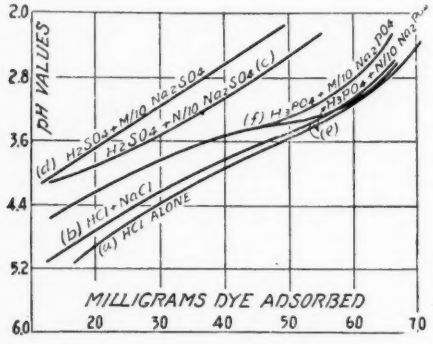


FIG. 7—*Effect of anions on the adsorption of Lake Scarlet R*

It is also evident that less dye was adsorbed from hydrochloric acid baths when sodium chloride was added and this is likewise in agreement with the theory. In a similar way, less dye was adsorbed when sulphuric acid was substituted for hydrochloric acid in the dye bath, although the effect was not as marked for sulphuric acid alone as for hydrochloric acid plus sodium sulphate, because in the latter case the concentration of sulphate ions was greater and the two experiments are not comparable. It is often the custom among colloid chemists to regard phosphate solutions as a source of trivalent phosphate ions.[23 24] Were this true we might therefore expect phosphate to be a more effective restraining agent than divalent sulphate, assuming the valence rule. The data, however, show that phosphate is much less effective. The reason for this perhaps unexpected result probably

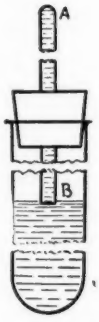


FIG. 8—*Diffusion tube*

lies in the fact that in phosphate solutions we do not really have trivalent ions to any appreciable extent. Phosphoric acid dissociates very largely as a monobasic acid, slightly as a dibasic acid, and only very weakly as a tribasic acid. The effective valence of the anions in phosphate solutions should therefore be between one and two, and we should expect the curve for phosphoric acid to lie between the curves for hydrochloric and sulphuric acid. Inspection of *Fig.* 6 shows that this is indeed the case. Lake[25] has reported that the addition of sodium phosphate to dye baths containing hydrochloric acid almost completely prevented the taking up of acid dyes by wool. He ascribed the effect to the trivalent phosphate ion. As Lake used an excess of disodium hydrogen phosphate, solutions of which have a pH value of about 9.2, it seems probable that the very considerable change in hydrogen ion concentration resulting from the addition of this salt was, to a large extent, the cause of the restraining action that he reported.

An attempt was made to use potassium ferri and ferro

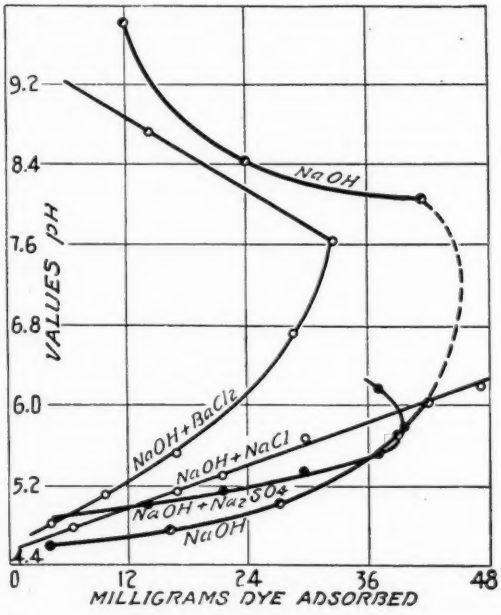


FIG. 9—*Adsorption of Methylene Blue by wool*

cyanides as sources of trivalent and tetravalent anions but in each case these substances reacted with the dye, and the experiments could not be completed.

To show that the phenomena observed in the case of Lake Scarlet R were general for the acid dyes, another series of experiments was performed with Du Pont Orange II. This dye can be titrated readily with titanium chloride in the presence of Rochelle Salt and is therefore easily determined in solution. In each of the experiments in this series one gram of wool was boiled for forty-five minutes in a dye bath (250 cc.) containing seventy-five milligrams of dye plus the various addition agents specified in Table IX. In each of the sets of experiments comprising Table IX, however, the total amount of sulphate or phosphate was kept approximately the same and only the pH of the dye baths was varied; in this regard the series differs from the one with Lake Scarlet R. Thus in the two sets of experiments with sulphuric acid and sodium sulphate, the quantity of acid and the quantity of salt were each varied, but their total was kept constant at 25 cc. of either N/10 or M/10 sulphate solution

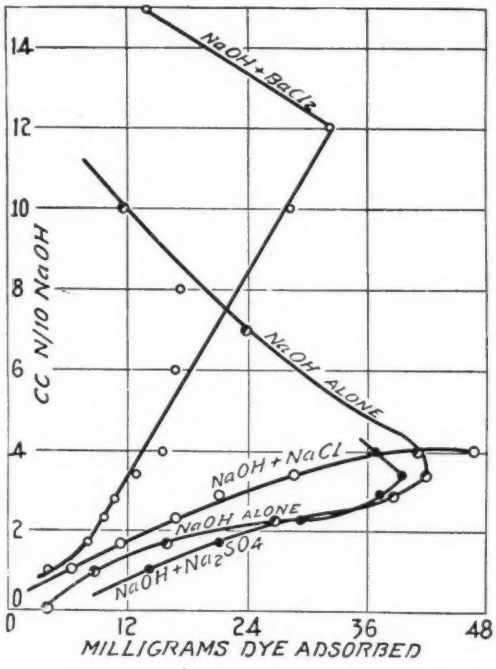


FIG. 10—*Adsorption of Methylene Blue by wool*

TABLE IX

THE EFFECT OF ADDITION AGENTS ON THE ADSORPTION OF ORANGE II

Hydrochloric Acid Alone

cc. N/10 HCl	Final pH	Mgs. Dye Adsorbed
0.5	4.34	28.8
0.7	4.23	33.6
0.8	4.16	34.8
1.0	4.03	35.4
1.3	3.70	47.0
1.5	3.60	51.7
2.0	3.38	54.5
3.0	3.18	59.2
6.0	2.76	63.0
10.0	2.49	69.7

Hydrochloric Acid Plus Sodium Chloride

cc. N/10 HCl	cc. N/10 NaCl	Final pH	Mgs. Dye Adsorbed
0.3	24.70	4.88	16.4
0.6	24.40	4.68	20.2
0.8	24.20	4.30	29.0
1.0	24.00	3.84	35.0
2.0	23.00	3.56	48.0
3.0	22.00	3.29	57.0
4.5	20.50	2.97	61.7
7.0	18.00	2.68	63.5
10.0	15.00	2.45	66.7

Sulphuric Acid Plus Sodium Sulphate

cc. N/10 H_2SO_4	cc. N/10 Na_2SO_4	Final pH	Mgs. Dye Adsorbed
0.3	24.70	4.12	13.5
1.0	24.00	3.83	25.0
2.0	23.00	3.50	29.9
3.0	22.00	3.27	36.1
4.5	20.50	2.96	42.5
7.0	18.00	2.71	48.6
11.0	14.00	2.32	53.2
cc. N/10 H_2SO_4	cc. N/10 Na_2SO_4	Final pH	Mgs. Dye Adsorbed
0.15	24.85	4.08	13.5
1.50	23.50	3.24	28.8
5.50	19.50	2.33	45.9

Phosphoric Acid Plus Disodium Hydrogen Phosphate

N/10 H_3PO_4	N/10 Na_2HPO_4	Final pH	Mgs. Dye Adsorbed
12.4	12.60	4.80	9.6
12.5	12.50	4.75	13.0
12.6	12.40	4.57	14.0
12.9	12.10	4.47	15.3
13.5	11.50	4.00	24.5
14.0	11.00	3.82	31.0
15.5	9.50	3.44	44.0
17.0	8.00	3.30	55.0
18.0	7.00	3.22	57.2
19.2	5.80	3.05	60.8
20.7	4.30	2.89	61.0
23.7	1.30	2.65	65.6
25.0	0.00	2.52	67.5
M/10 H_3PO_4	M/10 Na_2HPO_4	Final pH	Mgs. Dye Adsorbed
12.83	12.17	4.30	18.4
15.34	9.66	3.08	55.1
23.67	1.33	2.28	66.0

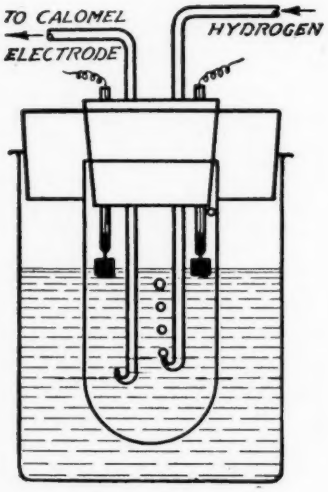


FIG. 11

in a dye bath of 250 cc. The results are plotted in *Fig.* 7.

Attempts were made to determine the effect of divalent and trivalent cations, but the three (barium, magnesium, and aluminum) whose chlorides were added to the dye bath caused the dye to precipitate. It is well known, however, that when the calcium or magnesium salt of an acid dye is soluble, it will be taken up more readily than the sodium salt of the same dye.

At low concentrations the effect of such anions as sulphate on the adsorption of an acid dye by wool is due, as stated before, to adsorption of the inorganic anion in place of some of the dye. It is easily possible, however, that at higher concentrations of sulphate the solubility of the dye may be diminished so that its tendency to be adsorbed may actually be increased. In other words, the restraining effect of sodium sulphate on acid dyes may pass through a maximum as the sulphate concentration is increased.

To test this point a series of experiments[26] was carried out with dye baths which contained more sulphate than was the case previously. General conditions otherwise were kept as before. Each dye bath contained seventy-five milligrams of Du Pont Orange II and five cc. of N/10 sulphuric acid in 250 cc. One gram of wool was boiled in each bath for forty-five minutes.

The partially exhausted baths were then analyzed for unadsorbed dye. Although equal amounts of acid had been added to all the baths, the hydrogen ion concentrations after dyeing were not the same throughout, probably because of the influence of the salt on the dissociation of the acid. Final hydrogen ion concentrations in this particular series of baths could not be determined by means of the hydrogen electrode because of some peculiar influence of the dye under these conditions. It was therefore necessary to resort to an indirect method for securing pH values. Mixtures of sodium sulphate and sulphuric acid were prepared corresponding to the concentrations existing in the dye baths and the pH values of these solutions were secured. The values thus obtained were applied to the dye baths.

In order that the effect of changing the sodium sulphate concentration may be determined, it is necessary that all other variables shall be controlled. The final pH values must therefore be the same throughout the series or the results must be corrected to a constant pH value. The latter method was employed and all adsorption values were corrected to a pH of 3.50, as follows: It was assumed that, over the short range of pH involved, the curves between milligrams of dye adsorbed and pH values were straight lines like those shown in *Fig.* 7 for N/10 and M/10 sodium sulphate and that they were approximately parallel to these lines. For each of the baths a point was placed on *Fig.* 7 at the position representing the milligrams of dye adsorbed and the pH as found. Lines were then drawn through these points parallel to the curve for M/10 sodium sulphate. The intersection of these new lines with the pH line equal to 3.50 gave, by direct reference to the X axis, the corrected milligrams of dye adsorbed.

Another method of comparing the effects of various concentrations of sodium sulphate is to compute the restraining action of the sulphate in each case by comparison with the adsorption curve in *Fig.* 7 for hydrochloric acid alone at the same pH value. The results by both methods are given in Table XI. It is plainly evident that the restraining action of the sodium sulphate passed through a maximum as its concentration was increased.

TABLE XI

THE EFFECT OF SODIUM SULPHATE OF THE ADSORPTION OF ORANGE II

No.	Bath Conc. Na_2SO_4	pH	Mgs. Dye Adsorbed	Mgs. Dye Adsorbed Corrected	Method 2 Restraining Effect of Sulphate
1	N/100	3.5	29.9	29.9	21.1
2	N/50	3.2	28.8	24.1	33.4
3	N/10	3.1	17.0	10.1	42.5
4	N/5	3.2	14.0	9.9	43.5
5	N	3.5	12.2	12.4	38.8
6	2N	3.6	27.3	28.4	21.7
7	3N	3.6	41.5	43.4	7.5
8	4N	3.7	47.1	50.8	−0.6

In order to show that the effect of the sulphate in the higher concentrations was actually due to a decrease in solubility, portions of baths 5, 6, 7, and 8 were placed in collodion thimbles after dyeing and immersed in solutions of sodium sulphate of the same concentrations as those inside the thimbles. At the end of forty-eight hours No. 5 showed strong diffusion, 6 slightly less, and 7 and 8 only very slight diffusion with 8 less than 7, showing that the sodium sulphate had lowered the solubility of the dye.

Basic Dyes

Experiments were next undertaken with basic dyes of which Methylene Blue was chosen first as a typical example. This dye proved to be a convenient one because it may be determined readily and accurately by titration with titanium chloride. Diffusion experiments[27] (*Fig.* 8) indicated that the dye forms true solutions in either neutral, weakly acid or weakly basic solutions. In more strongly basic solutions, however, the dye forms a suspension and may be almost completely precipitated as the alkalinity is increased further.

By following the general procedure that was employed with the acid dyes, the amount of methylene blue taken up by wool in the presence of addition agents was determined. As in the previous work, one gram of wool was boiled for forty-five minutes in a dye bath of 250 cc. containing seventy-five milligrams of dye.

The first step was to ascertain the relation between hydrogen ion concentration and the amount of dye adsorbed. The data given in Table XII and in *Fig.* 9 represent the results obtained. It will be noted that the effect of a change in pH is not so marked with this dye as it was in the case of acid dyes. It is also apparent that the total amount of base used is as important as the final pH of the solution. To bring out this point the curves in *Fig.* 10 have been prepared by plotting total base added as ordinates instead of pH. Since the amount of dye adsorbed at first is practically proportional to the total base added, it seems probable that the dye base is taken up more strongly than its hydrochloride and that the adsorption of dye is roughly proportional to the amount of free dye base present.

A striking feature of each of these curves is the presence of a point of maximum adsorption. There are apparently two reasons for such a point. It will be recalled from the experiments on diffusion previously described that methylene blue passes from true to colloidal solution as sodium hydroxide is added and that when the latter is present in fairly large quantities, flocculation occurs. It is probable that sodium hydroxide removes hydrochloric acid from the methylene blue and sets free the dye base which is insoluble in water and which remains in suspension.

The dye now being distinctly in colloidal solution, a modification of the dyeing process results. All dyes behave like the substantive or direct dyes if their solutions become colloidal. For this reason, Methylene Blue, as soon as it has been rendered colloidal by the addition of sodium hydroxide, acts as a substantive dye and no longer behaves as a true basic dye. Briggs and Kakiuchi and Briggs and Woodward[28] have shown that the adsorption curves for substantive dyes pass through a maximum as the concentration of electrolytes is increased. Since Methylene Blue is colloidal in alkaline solution, it is to be expected that it would behave in a similar way. This supposition is confirmed by the data given in Table XII.

The other factor tending to produce a maximum point in the curves, is the action of the sodium hydroxide on the wool. The samples dyed at the higher concentrations of alkali showed very appreciable decomposition.

In those experiments the Methylene Blue was adsorbed strongly by the hydrogen electrode and after a few minutes the readings of the electrode showed a gradual falling off. Table XII contains a series of readings made under such conditions.

TABLE XII

THE ADSORPTION OF METHYLENE BLUE HYDROXIDE

In the Presence of Sodium Hydroxide

cc. N/10 NaOH	Final pH	Mgs. Dye Adsorbed
0.0	4.50	4.0
1.0	4.72	9.0
1.7	4.73	16.3
2.3	5.03	27.0
2.9	5.69	38.7
3.4	6.02	42.0
4.0	8.05	41.5
7.0	8.40	23.7
10.0	9.81	11.9

In the Presence of Sodium Chloride

cc. N/10 NaOH	cc. N/10 NaCl	Final pH	Mgs. Dye Adsorbed
1.0	25.00	4.80	6.4
1.7	25.00	4.80	11.6
2.3	25.00	5.12	17.1
2.9	25.00	5.29	21.4
3.4	25.00	5.66	28.9
4.0	25.00	6.18	46.9

In the Presence of Sodium Sulphate

cc. N/10 NaOH	cc. N/10 Na_2SO_4	Final pH	Mgs. Dye Adsorbed
1.0	25.00	5.00	14.2
1.7	25.00	5.13	21.4
2.3	25.00	5.35	29.4
2.9	25.00	5.48	37.6
3.4	25.00	5.78	39.6
4.0	25.00	6.17	37.1

In the Presence of Barium Chloride

cc. N/10 NaOH	cc. N/10 $BaCl_2$	Final pH	Mgs. Dye Adsorbed
1.0	25.00	4.80	4.3
1.7	25.00	4.96	8.4
2.3	25.00	5.08	9.9
2.8	25.00	5.05	10.8
3.4	25.00	5.17	13.2
4.0	25.00	5.35	15.6
6.0	25.00	5.50	17.0
8.0	25.00	6.06	17.6
10.0	25.00	6.70	28.5
12.0	25.00	7.61	32.3
15.0	25.00	8.72	14.2

TABLE XIII

Voltage reading	0.460	0.562	0.560	0.558	0.558	0.556	0.553	0.548
Time in minutes	1	2	3	5	7	10	20	27

"Time in minutes" means minutes elapsed from the time hydrogen was first started bubbling through the solution under test. The voltage rises quickly, remaining at a nearly constant value for several minutes and then gradually falls off again. This secondary decline is probably due to an adsorption of the dye by the electrode. By treating the hydrogen electrode with chromic acid cleaning mixture after each determination, the film of dye is stripped off and the surface renewed.

If the theoretical hydrogen ion concentrations of the dye baths given in Table XII are calculated, it will be found that in all cases the observed pH values are lower than one would expect, even though one allows for the hydrochloric acid liberated from the Methylene Blue. In order to make sure that the dye had not affected the hydrogen electrode and caused it to give consistently low readings, the apparatus shown in *Fig.* 11 was prepared. In this device the hydrogen electrodes were partially immersed in distilled water contained in a collodion sac (S). The latter was then immersed in a dye bath of Methylene Blue whose pH value had been previously determined in the usual way. The bath chosen was a strongly alkaline one which had gone almost completely colloidal on boiling. Alkali began at once to pass into the sac and the rate of diffusion was followed by observing the change in the potential of the electrode. The dye did not diffuse through the collodion membrane so its possible effect on the electrodes was eliminated. The final pH value obtained in this way corresponded closely (8.72 and 8.79) with the value obtained in the usual manner where the electrodes were immersed dirctly in the dye bath.

One gram of wool was boiled forty-five minutes in 250 cc. of sodium hydroxide solution containing 15 cc. of N/10 sodium hydroxide. The free base left after this treatment was titrated with hydrochloric acid using phenolphthalein as indicator. It was found that only 5 cc. of free base remained. The action of the alkali on the wool and its removal by the latter will therefore account for the high concentrations of hydrogen ion found in the experiments on Methylene Blue.

Summary

1. The process of dyeing wool with acid and basic dyes has been investigated from the standpoint of the adsorption theory of dyeing as formulated by Pelet-Jolivet and Bancroft.

2. The effect of dyes on the adsorption of acids by wool and of acids on the adsorption of dyes has been determined quantitatively for typical acid dyes.

3. It has been shown that the taking up of dyes is a case of adsorption and that the amount of dye adsorbed varies continuously with a change in the hydrogen ion concentration of the dye bath. No evidence of chemical action between dyes and wool has been found.

4. The use of the hydrogen electrode has made it possible to control a hitherto neglected variable.

5. The action of assistants has been studied and has been found to be strictly in accord with the theory.

The writers take this opportunity to express their thanks to Professor W. D. Bancroft for his unfailing interest and help.

This work was made possible by a fellowship grant from E. I. du Pont de Nemours & Co., to whom our thanks are also due.

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[20] Behrend: Zeit. phys. Chem., **11,** 462 (1893). The potential of a silver electrode against any solution in which it is placed is a function of the silver ion concentration of the solution. If one measures the potential of a silver electrode immersed in a chloride solution to which silver nitrate is being added, the curve shown in Fig. 3 is obtained. So long as silver chloride is precipitated, the silver ion concentration of the solution is extremely small and roughly constant. As soon as an excess of silver nitrate is added, however, the concentration of the silver ions in the solution rises rapidly and a sudden change in the potential of the electrode occurs. It is thus possible to determine chlorides in colored solutions, provided that no other substance is present which forms a precipitate or a complex ion with the silver nitrate. In measuring the potential of the silver electrode it is, of course, necessary that the calomel electrode be connected with the solution through an ammonium nitrate or similar salt bridge to prevent contamination of the solution with potassium chloride from the electrode.

[21] "Die Theorie des Färbeprozesses" (1910).

[22] Jour. Phys. Chem., **20,** 76 (1916).

[23] Lake: Jour. Phys. Chem., **20,** 786 (1916).

[24] Compare Loeb: Jour. Gen. Physiology, **3,** 248 (1920).

[25] Jour. Phys. Chem., **20,** 786 (1916).

[26] We are indebted to W. W. Paddon for aid in this series of experiments.

[27] A glass tube (AB) of about 2 mm. inside diameter and sealed at the top is filled with distilled water and then placed with its open end just below the surface of the dye solution to be tested. If the dye is in true solution, diffusion will be evident in a few hours and after several days the color will have extended nearly to the top of (AB). Colloidal suspensions show little or no diffusion. In case electrolytes have been added to the dye bath, the tube (AB) should be filled with an equivalent solution of these electrolytes instead of with pure water, to prevent any change in the condition of the dye as it diffuses up the tube. It should be recognized that between true solutions and colloidal suspensions we may and do have all degrees of combination of the two states. Part of the dye may be in true solution while the rest is colloidal.

[28] Results will be published in a subsequent paper.

Thomas Eccleston, formerly with the Bradford Dyers' Association, Bradford, R. I., has been appointed suuperintendent of the Lewiston Bleachery & Dye Works, Lewiston, Me., where he succeeds the late P. J. Gainey.

The White Star Chemical Company, New York, N. Y., has been incorporated with a capital of $30,000, to manufacture chemicals, dyes, etc. The incorporators are H. K. Copeland and J. H. Ennis, Jr. The company is represented by W. J. Carey, 220 Broadway, New York City.

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LAURANCE T. CLARK
Managing Editor

Published biweekly by
HOWES PUBLISHING CO., INC.
4109 Woolworth Building, New York City

A. P. HOWES, *President* E. S. PREDMORE, *Secretary*

Subscription price $5.00 per year: Canadian $5.50; foreign $6.00.

Vol. XII January 1, 1923 No. 1

RESEARCH AND THE UNIVERSITIES

ATTENTION was directed not so long ago to the report for the academic year ended June 30, 1921, in which Dr. F. J. E. Woodbridge, dean of the Faculties of Political Science, Philosophy and Pure Science at Columbia University, discussed the place for research in university policy and organization. This report, declares Alfred D. Flinn, of the Engineering Foundation and the National Research Council, contains many arresting statements. Words from a scholar so highly placed in the university realm challenge consideration, for they must have been written with the purpose of influencing action by thoughtful persons. Manifestly some of the Dean's words are addressed to supporters of research and learning outside the universities as well as to the officers, trustees and faculties of the universities.

Commenting upon inquiries as to how much research is done in universities, Dr. Woodbridge states, "I do not like to answer in any way that leaves the impression that the researches of a professor in the graduate school do not have the most intimate relation to his work as a teacher, but need some extraordinary encouragement. Yet that impression is current and is encouraged, I fear, by what we are getting in the habit of calling research foundation—as if the graduate school were not itself a research foundation of the first importance. It is an impression which we should do everything in our power to dispel. It can work very great mischief.

"I am quite convinced that the university is a far better place for research than any foundation set up for the purpose exclusively. New students coming from all parts of the world, seeking an opportunity to prove their worth and bringing ever fresh enthusiasm, keep the enterprise of learning continually invigorated with new stores of energy."

Dr. Woodbridge in the first quotation evidently is making a statement of fact. The unfortunate condition and position of research in some universities of America to which he alludes has been observed with apprehension by the National Research Council, Engineering Foundation and other research foundations. Foundations related to the technological professions and industries, at least, have been conscious that the numbers of real research men coming from the universities—men with the inborn traits and thorough training needed for research—have been inadequate for the demands. It is not strange, therefore, that some of these foundations have been endeavoring to co-operate with the universities in finding and training young men with native ability for research. Not funds alone, but helpful services have been proffered in this endeavor to create in the universities a larger place for research and make it a vital element of university life. When university officers shall have given research its large and rightful place in the halls of learning, the promotive endeavors of the foundations can be discontinued; but the cordial co-operation should go on, although with different objects.

There is a service for research, Mr. Flinn reminds us, which belongs peculiarly to the universities, but there is also as distinctly a work for the foundations. These two are not antagonistic, but supplementary. There are researches which can best be pursued in university laboratories and libraries; there are others for which the background and resources of an industry or of a research institute are essential.

In the Chinese aniline dye market indigo is the strong feature and has recovered somewhat in price. German indigo is selling at 53 Shanghai taels per picul (133 1/3 pounds), while the best quality of American indigo sells at 50 taels. French interests are not in the market at present and it is reliably reported that France is to sell aniline products through Germany, with a later division of territory.

The Keene Chemical Company, New York, N. Y., has been incorporated with a capital of $100,000, to manufacture and deal in chemicals, dyes, etc. The incorporators are S. M. Morecy, J. Weissbaum and E. H. Barker. The company is represented by S. S. Winter, 261 Broadway, New York City.

The Hulton Dyeing Company, Philadelphia, have filed plans for the erection of a new one-story addition to their plant in Frankford. It is understood that construction will begin at once.

Salembier & Villate, Inc., New York, was recently incorporated to deal in silks and textiles. Capital, $1,000. The incorporators are T. A. O'Callaghan, J. G. Lynch and J. B. Breckenridge.

Removal of Italian Dye Exports Ban Stimulates Domestic Incorporations

No Increase in Import Duties—Rise in German Dye Prices Complicates Matters—Possible Recovery of the Mark—Stiff Competition for Italian Color Works—Consumers Benefit—More Business for American, British and French Color Makers

By RAFFAELE SANSONE

Genoa, December 8.
Special to The Reporter.

THE lifting of the ban on the exportation of dyestuffs from Italy has encouraged a greater activity on the part of the importers and exporters of coloring matters, resulting in the formation of a certain number of new firms. Among the most important of these is the Importazione, Esporazione Materie Coloranti, Prodotti Chimici, Societa Anonima, having a capital of 150,000 lire in 150 shares of 1,000 lire. This new firm also conducts the exportation of coloring matters, showing that the founders count on a certain amount of speculation, facilitated by the continual oscillations in the foreign exchange, to make ends meet in case the domestic market gives them unsatisfactory results.

The recent rise in the prices of dyestuffs in Germany, and the probability of a recovery in the value of the German mark, complicates, however, the importation of German colors other than the reparation colors, and facilitates business with American, English and French color manufacturers. It is notable that the removal of the color export ban was not followed by any increase in the importation customs on these products.

The Italian color works, on their part, have been obliged to contend with still stronger competition from the imported coloring matters, whereas the cotton, wool, silk, hemp, jute, paper and leather dye works benefited by the situation, obtaining more easily whatever products were not supplied from the Italian Government stocks.

Through special dispositions of the Italian ministry, the Italian lira gained strongly in value, bringing the United States dollar from 24.50 lire to 20 lire, and the English pound sterling from 106 lire to 91.10 lire, strongly reducing the lira values of all quotations of American and English products, and rendering less profitable the business of the exporters, who, if the advance continues, will lose much of their present business, it being less convenient to export the goods produced in Italy.

A commercial conference between Italy and France has arranged specially low import tariffs to encourage a more active exchange of products between these two

TABLE I

	November 8		December 8	
	(Lire)	(Dollars)	(Lire)	(Dollars)
Naphthol Yellow	40,000—65,000	1,538—2,500	40,000—65,000	2,000—3,250
Auramine	60,000—70,000	2,307—2,692	60,000—70,000	3,000—3,500
Orange II	22,000—25,000	846— 961	22,000—25,000	1,100—1,250
Nigrosine, water soluble	28,000—35,000	1,076—1,345	28,000—35,000	1,400—1,750
Nigrosine, soluble in alcohol	30,000—38,000	1,153—1,461	30,000—38,000	1,500—1,900
Sulphur Black	7,000— 9,750	269— 375	6,750— 9,750	337— 487
Acid Black	30,500—34,500	1,173—1,326	30,000—35,000	1,500—1,750
Direct Black	29,500—35,000	1,134—1,345	30,000—36,000	1,500—1,800
Chrome Black	34,000—37,000	1,307—1,423	34,000—38,500	1,700—1,925
Methylene Blue	75,000—90,000	2,884—3,461	75,000—90,000	3,750—4,500
Direct Blue	24,500—28,000	942—1,076	24,500—28,000	1,225—1,400
Sulphur Blue	33,500—37,500	1,288—1,442	33,500—38,000	1,675—1,900
Malachite Green	75,000—90,000	2,884—3,461	75,000—90,000	3,750—4,500
Acid Green	60,000—70,000	2,307—2,692	60,000—70,000	3,000—3,500
Direct Green	42,000—54,500	1,615—2,096	41,000—54,500	2,050—2,725
Bismarck Brown	35,000—41,500	1,345—1,596	35,000—42,000	1,750—2,100
Magenta (Fuchsine) Crystals	70,000—80,000	2,692—3,076	70,000—80,000	3,500—4,000
Eosine	50,000—75,000	1,923—2,884	50,000—75,000	2,500—3,750
Ponceaux	28,500—35,500	1,096—1,288	28,500—35,000	1,425—1,750
Methyl Violet	65,000—80,000	2,500—3,076	65,000—80,000	3,250—4,000

TABLE II

	(Lire)	(Dollars)	(Lire)	(Dollars)
	November 8		December 8	
Acetate of alumina	1,600	61	1,600	80
Chrome alum	3,000	115	3,500	175
Bichromate of potash	5,700	219	5,900	295
Ferrous sulphate	500	20	500	25
Copper sulphate	2,100	80	2,400	120
Tartaric emetic	12,000	461	12,000	600
Aniline oil	10,000	384	13,500	675
White refined glycerine	9,000	346	8,800	440
Glucose, 45 deg. Be	3,900	150	3,900	195
Hydrogen peroxide	2,100	80	2,100	105
Tannic acid, 60 per cent	20,000	769	20,000	1,000
Tartaric acid, crystals	12,000	461	12,500	675
Acetic acid, 30 per cent	2,200	84	2,200	110
Hydrochloric acid, 20 to 21 deg. Be	300	11	300	15
Formic acid	7,500	288	7,500	375
Lactic acid, 80 per cent	4,000	153	6,000	300
Alum	1,000	38	1,000	50
Ammonia, 22 deg. Be	1,450	55	1,450	72
Bisulphite of soda, 32 deg. Be	380	14	380	19
Chlorate of potash	3,200	123	3,200	160
Chloride of ammonit	4,000	153	4,000	200
Bleaching powder	900	34	900	45
Nitrite of soda	2,950	113	2,950	147
Yellow prussiate of potash	22,000	846	22,000	1,100
Yellow prussiate of soda	13,000	500	12,900	645
Caustic soda, 70/72	2,100	80	2,100	105
Silicate of soda, 140 deg. Tw	1,000	38	1,000	50
Sodium sulphide	2,800	107	2,300	115
Logwood extract	7,000	269	8,000	400
Yellow dextrine	3,700	142	3,300	165
White dextrine	3,950	151	3,400	170
Farina	2,700	103	2,550	127
Kordofan gum	8,000	307	8,000	400
Indigo, 25 per cent	23,000	884	23,000	1,150
Beta-naphthol	19,000	750	19,000	950
Industrial castor oil	6,500	250	6,750	337

nations, and this also will certainly have its effect in the importations of colors from the latter country.

The Demand for Colors

The demand continued good on the Italian market for colors for dyeing wool, where the fastest colors found a strong sale, especially with works in Piedmont, Lombardy, Veneto and Tuscany. Cotton dyes were also strongly purchased, and among these were most especially Direct Sky Blues, Direct Navy Blue, Direct Browns such as Cathechine Diamine, Direct Cutch Brown, Direct Orange Brown, Direct Black BH, Chrysophenin, Direct Bronze, Direct Violet, Direct Orange, Ferica BN and GN, etc. With silk dyes the demand was less pronounced. A certain demand was noted for dyes for artificial silk, textilose, paper and leather.

Prices of Coal Tar Dyes

The quotations of reparation dyes in Table I, per ton in lire and dollars, show the difference in the dollar and lira prices at the moment of writing, in comparison with the prices prevailing on November 8 (the dyeing being delivered in kegs of from 25 to 50 kilos).

Mordants, Assistants, Dyehouse Products

The greater activity of the dye works, despite the lower foreign exchange, brought about an increase in the prices of some of the products, and especially of chrome alum bichromate of potash, copper sulphate, aniline oil, tartaric acid crystals, lactic acid, Logwood extract, industrial castor oil, etc. In some cases, and when the products had to be imported, a fall in price followed. For this reason the Italian consumers and merchants only placed

orders abroad when compelled to do so. The situation more especially aided the national producers, most of whom worked in full time.

Some of the lira and dollar quotations are given, per ton at Milan, in Table II.

Private Dyehouse Quotations

Some private quotations for dyestuffs at Genoa were as follows, per kilo, showing how these competed against the War Reparation products: Direct Black, 32 to 35 lire; Nigrosine Crystals, 26 to 30 lire; Chrome Black in powder, 34.50 to 36 lire; Direct Green, 50 to 54 lire; Orange II, 22 to 26 lire; Methylene Blue, 75 to 90 lire; liquid Fustic extract, 8 to 8.50 lire; Logwood extract, 8 to 8.50 lire; Hematite crystals, 12 to 13 lire.

DU PONT DEVISES A DYESTUFF TRADE-MARK FOR CHINA

The dyestuffs department of the E. I. du Pont de Nemours & Co. has hit upon an interesting way to gratify the Chinese love of "cumshaw"—i. e., something for nothing—and at the same time provide a secure, rust-proof fastening for their indigo shipments to Chinese markets. The indigo is shipped in one-picul kegs (133 1/3 pounds), being calculated a suitable burden for one Chinese back. A copper seal is fastened over the bung in the filling hole by means of screws, which are then soldered. The seal prevents tampering with or adulteration of the contents and, being of copper, is not affected by moisture. At the same time it serves as a very acceptable prize for the Chinese in the dyehouses where the indigo is used.

The seal is circular in form and bears upon its face the familiar Du Pont oval. This time, however, the oval encloses two smaller ovals, one above the other; the upper oval contains the name DU PONT as in the company's trade-mark, while the lower surrounds an inscription in Chinese characters. There are likewise Chinese characters on either side of the two small ovals.

The characters in the lower oval are "Hung Hsin Yang Hong," meaning "constantly reliable foreign firm." The characters on either side of the two small ovals are "Shang" and "Mei," which means "American corporation."

The bulk of the dyes imported into China consists of artificial indigo, according to Julean Arnold, U. S. Commercial Attache at Shanghai, of which probably 90 per cent is distributed among the Chinese consumers in the form of artificial indigo paste containing 20 per cent indigotin. Six months ago the average selling price of artificial indigo paste containing not over 20 per cent indigotin was about 75 taels, or $56 (gold), per picul of 133 1/3 pounds. To-day the same article is selling at about 40 taels, or $30 (gold), per picul. This latter price is approximately the same as the pre-war values. The reduction is due, in the main, to the heavy importations from German manufacturers whose production costs, owing to the German exchange, are much lower than those in America.

The annual imports of artificial indigo into China are about 11,000,000 taels in value, or $8,580,000 (gold). When the selling price rises much above 40 taels per picul (which at the current rate of exchange is equivalent to $23 gold per 100 pounds), the Chinese take to the greater use of natural indigo, which is produced in China and also imported from India. It appears that Chinese trade cannot afford to use natural indigo when the artificial product can be purchased in the proximity of 40 taels per picul.

The selling of indigo dyes in China can be done successfully only through an organization thoroughly conversant with the details of this business. At present the Swiss, French and American interests able to compete with the German product are manufacturers handling their own products through their own organizations in the field. The bulk of the trade will go to those manufacturers who are able to supply the material at the lowest price and in a form acceptable to the consumer in the interior of the country. It is estimated that 60 per cent of the world's production of artificial indigo is consumed in China.

HARING & STEVENS BUY EAST JERSEY PIPE COMPANY

Announcement has been made that the Haring & Stephens Company, Paterson, N. J., has purchased the machine shop of the East Jersey Pipe Company, together with the latter company's entire equipment, stock, patterns, patent rights and good-will. The East Jersey Pipe Company was well known to the trade as a producer of Hercules electro hydro-extractors. These will now be made by the purchasing company.

The personnel of the Haring & Stephens Company, with headquarters at 1527 Kentucky Avenue, Paterson, consists of J. L. Haring, formerly sales manager, and H. H. Stephens, formerly general manager, of the East Jersey Pipe Company, both of whom are therefore familiar with the manufacture and sale of the hydro-extractors. Mr. Haring is a mechanical engineer with long experience in the design and construction of dyeing, finishing and special machinery and centrifugal extractors. Mr. Stephens has had fifteen years' experience in the development of motor-driven extractors. He is a member of the American Society of Mechanical Engineers and the American Institute of Electrical Engineers.

With a capital of $100,000 the Dyecraft Corporation was recently formed by W. C. Hall and B. & W. Knoepfel to manufacture and deal in textile articles. The plant is located at the foot of Willow Avenue, North Bergen, N. J., where they are dyeing wool yarns and other materials.

Do You Guess or Know?

In dyeing, bleaching and finishing operations, the difference between knowing and guessing is largely a question of the extent to which efficient laboratory control is substituted for "rule of thumb" methods. One faulty operation may ruin thousands of dollars' worth of materials.

In order to function efficiently the laboratory must be complete and modern in every respect. To skimp expenditures on laboratory equipment is the acme of false economy.

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H Acid, Chromotropic Acid, Hydrosulphite of Soda, discharging and stripping compounds are among the more recent products of the company which are of interest to dyers.

Merrimac Chemical Company

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THE SUCCESS of the last exhibition was so pronounced that many of the exhibitors have already filed their applications for the coming Exposition.

Before the official allotment of space is made, however, the National Association of Hosiery and Underwear Manufacturers extends a most cordial invitation to all Knitting Machinery, Knitted Underwear and Outerwear Manufacturers of every character, Hosiery, Yarn and Mill Equipment makers, to participate in this exhibit and partake of the numerous benefits to be derived — new business — new friends — new ideas — renewal of old acquaintances; all essential to a successful and up-to-date business house.

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The big obvious need of this country to-day is psychological—the disposition to go ahead. We have here a vast ability to produce, and a vast ability to consume, the products of industry. Potentially, Supply and Demand are pretty well matched. The main trouble is that people don't demand enough things to justify industry in doing its utmost to produce.

The result is that a great amount of energy is being spent on trying to get a lion's share of the existing demand, and not enough is spent on trying to create the demand so there will be enough to keep everybody busy supplying it.

This brings about a period of keen competition. It means that everybody must work harder and accept less in order to overcome the sales resistance of a curtailed demand.

Demand is largely a created thing. The actual needs of humanity are only a fraction of the general demand. It is always a simple matter to get along with less than one would like to have. When the public gets a streak of economy it curtails the demand for everything that is produced.

Advertising is a prime mover in creating business. It rouses people out of lethargy, makes them want to live more fully, and to possess the means of living more comfortably and more enjoyably.

When sales are hard to get, then most people who have things for sale increase their efforts to sell. The harder they try to sell, the harder their competitors try to sell. But no amount of selling effort—in the usual sense of the word—can create demand; it can only take advantage of the demand that has been otherwise created.

Advertising and Selling ought to be considered as "fifty-fifty" in importance. Advertising creates the consumer demand. Selling connects this demand with the supply. Each needs the other to make its work complete.

[Published by the American Dyestuff Reporter in co-operation with The American Association of Advertising Agencies]

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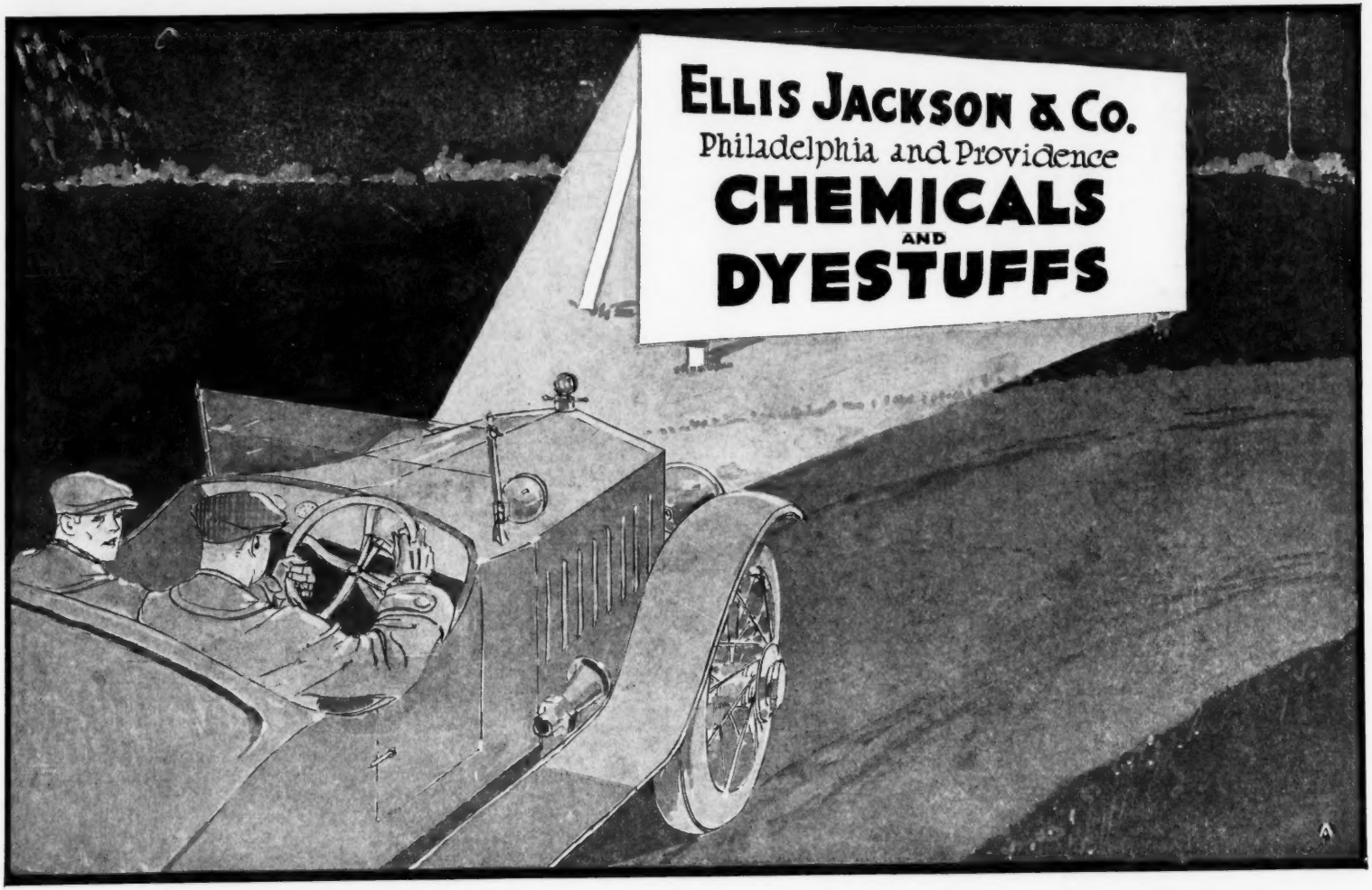
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